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LXXXI. *The Quantum Theory and Isotopes.* By J. W. NICHOLSON, F.R.S., Fellow of Balliol College, Oxford*.

IN the present paper, we group together various matters which are of importance in regard to the Quantum theory of spectra and of atomic structure. No definite arrangement is followed, the subjects being very much disconnected. But they all appear to be somewhat insufficiently dealt with in current accounts of the Quantum theory, and to be capable of a treatment which can make them suggestive of further progress in directions along which experimental work is now proceeding.

Pendulum-paths in an Atom.

Pendulum-paths, or "Pendelbahnen," are frequently referred to, as particular cases, in discussions of atomic theory. They are straight-line paths of an electron in an atom or molecule. The intensity of a spectrum line emitted when an atom passes between two stationary states is determined by the probability of the occurrence of these states among a large number of other equally likely states. The probability of the repeated formation of a state in which any electron describes a "Pendelbahn" is effectively negligible, so that such states, in themselves, are never likely to be effective in producing visible spectrum lines.

* Communicated by the Author.

and the equation of energy becomes

$$mc^2 \left\{ \frac{1}{\sqrt{1-\dot{x}^2/c^2}} - 1 \right\} - \frac{ve^2}{x} = -W,$$

W being the "total energy" in the Quantum theory sense.

The momentum $m\dot{x}$ is to be quantized according to

$$\oint m\dot{x} dx = nh,$$

where n is an integer. We find

$$1 - \frac{\dot{x}^2}{c^2} = m^2 c^4 / \left\{ mc^2 - W + \frac{ve^2}{x} \right\}^2.$$

When $x=0$, $\dot{x}=c$, which is therefore the velocity of passage through the nucleus. The oscillation takes place between the values of x making $\dot{x}=0$, or

$$m^2 c^4 = \left(mc^2 - W + \frac{ve^2}{x} \right)^2$$

leading to

$$-W + \frac{ve^2}{x} = 0, \quad -2mc^2,$$

or

$$x = \frac{ve^2}{W}, \quad -\frac{ve^2}{2mc^2 - W}.$$

These will be called $(\alpha, -\beta)$ respectively. Thus on reduction

$$\begin{aligned} m\dot{x} &= mc \left\{ \left(\frac{e^2 v}{x} + mc^2 - W \right)^2 - m^2 c^4 \right\}^{\frac{1}{2}} / \left(\frac{ve^2}{x} + mc^2 - W \right) \\ &= mc \left\{ \left(\frac{e^2}{x} - \frac{e^2}{\alpha} \right) \left(\frac{e^2}{x} + \frac{e^2}{\beta} \right) \right\}^{\frac{1}{2}} / \left\{ \frac{e^2}{x} + \frac{1}{2} e^2 \left(\frac{1}{\beta} - \frac{1}{\alpha} \right) \right\} \\ &= 2mc \sqrt{\alpha\beta} \cdot \sqrt{(\alpha-x)(\beta+x)} / \{ 2\alpha\beta + x(\alpha-\beta) \}. \end{aligned}$$

The quantizing condition becomes, since x ranges from α to $-\beta$ and back, in a complete period,

$$2 \int_{-\beta}^{\alpha} m\dot{x} dx = nh,$$

$$\text{or } \frac{nh}{4mc \sqrt{\alpha\beta}} = \int_{-\beta}^{\alpha} \frac{dx}{2\alpha\beta + x(\alpha-\beta)} \cdot \sqrt{(\alpha-x)(\beta+x)}.$$

Writing

$$x = \alpha \cos^2 \phi - \beta \sin^2 \phi,$$

$$\begin{aligned} \frac{nh}{4mc \sqrt{\alpha\beta}} &= 2(\alpha + \beta)^2 \int_0^{\pi/2} \frac{\sin^2 \phi \cos^2 \phi d\phi}{2\alpha\beta + (\alpha - \beta)(\alpha \cos^2 \phi - \beta \sin^2 \phi)} \\ &= 2(\alpha + \beta) \int_0^{\pi/2} \frac{\sin^2 \phi \cos^2 \phi d\phi}{\alpha \cos^2 \phi + \beta \sin^2 \phi} \\ &= 2(\alpha + \beta) \int_0^\infty \frac{t^2 dt}{(\alpha + \beta t^2)(1 + t^2)^2}, \quad (t = \tan \phi). \end{aligned}$$

The integral is easily evaluated as $\frac{\pi}{4} (\sqrt{\alpha} + \sqrt{\beta})^{-2}$, so that

$$\frac{nh}{4mc \sqrt{\alpha\beta}} = \frac{\pi}{2} \frac{\alpha + \beta}{\alpha + \beta + 2\sqrt{\alpha\beta}}.$$

But

$$\alpha + \beta = 2vmc^2 e^2 / \{W(2mc^2 - W)\},$$

$$\alpha\beta = v^2 e^4 / \{W(2mc^2 - W)\},$$

and finally,

$$\frac{nh}{2\pi mc} = ve^2 / \left\{ \sqrt{W(2mc^2 - W)} + \frac{W}{mc^2} (2mc^2 - W) \right\}.$$

This is the exact equation for W . If

$$W(2mc^2 - W) = X^2$$

we find

$$\frac{X^2}{mc^2} + X = \frac{2\pi vmce^2}{nh}$$

and the general value of X , and thence W , can be expressed. For a first approximation only,

$$\frac{nh}{2\pi mc} = \frac{ve^2}{c \sqrt{2mW}}$$

or

$$W = \frac{2\pi^2 m e^4 v^2}{n^2 h^2},$$

which is the value belonging to other orbits, to a first approximation. It is easy to show that the result is correct to any approximation.

The ratio of the lengths of path before and after passage through the nucleus is

$$(2mc^2 - W) / W,$$

or effectively

$$\frac{n^2 h^2 c^2}{\pi^2 e^4 \nu^2};$$

with the values $h = 6.5 \times 10^{-27}$, $e = 4.8 \times 10^{-10}$, this becomes of order

$$\frac{n^2}{\nu^2} \times 10^6;$$

with a Hydrogen atom in its normal state, $n = \nu = 1$. If its radius is of order 10^{-9} , the electron, after passing the nucleus, goes a distance of order only 10^{-14} , less than its own radius, but comparatively large in relation to the "radius" of the nucleus.

This distance is so small, in comparison with orbital dimensions in an atom, as to justify the statement that, in effect, the electron does not traverse the core of the atom—though, in its small penetration, it reaches a point from which it can again reach the nucleus with velocity c and return to its former stationary position on the other side, subsequently continuing its oscillations. The time spent on the far side of the nucleus is also very small. We may conjecture, therefore, that the spectrum formula may be derived by ignoring, even in this case, the influence of speed on mass, and by supposing that the electron starts with $\dot{x} = 0$ and *just* reaches the nucleus and returns on its path. We shall show that this is, in fact, the case. While the investigation is not of intrinsic importance in the simple Pendulum problem of the Hydrogen atom as such, it has important implications with regard to the corresponding problems for more complex atoms. For it will be clear to the reader that the conclusions derived in this special case have general features. In the first place, when, in a Pendulum problem, an electron "goes through" a nucleus, it will do so with the velocity of light, and for a negligible distance in comparison with the rest of its path. Secondly, the problem may be treated as though the electron stopped *at* the nucleus. The simplification thus introduced is very considerable, and nothing is lost by these suppositions except the fine structure of the spectrum lines—a secondary consideration in the elucidation of the structure of atoms more complex than Hydrogen, or of molecules.

The simple pendulum problem for the Hydrogen atom with a stationary nucleus, and without correction for variable mass of the electron, gives for the equation of energy

$$\frac{1}{2}m\dot{x}^2 = \frac{e^2}{x} - W,$$

and the quantum condition is

$$\oint m\dot{x} dx = nh$$

or

$$2 \int_0^{e^2/W} m\dot{x} dx = nh$$

by the preceding remarks, according to which the nucleus $x=0$ is one end of the path. Thus

$$\frac{1}{2}nh = \sqrt{2m} \int_0^{e^2/W} \sqrt{\left(\frac{e^2}{x} - W\right)} dx.$$

Writing $x = \frac{e^2}{W} \sin^2 \theta$,

$$\begin{aligned} \frac{1}{2}nh &= \sqrt{2m} \int_0^{\pi/2} \sqrt{W} \cdot \frac{\cos \theta}{\sin \theta} \cdot \frac{2e^2}{W} \sin \theta \cos \theta d\theta \\ &= e^2 \sqrt{\frac{2m}{W}} \frac{\pi}{2}, \end{aligned}$$

or

$$W = \frac{2\pi^2 m e^4}{n^2 h^2},$$

which establishes the validity of the procedure. In general, in such paths, we may say further that the influence of the velocity on the mass is unimportant except for fine structure of the lines.

A few remarks on the penetration of the nucleus by an electron are perhaps desirable at this point. It is customary to speak of nucleus and electron as though they were, in a sense, hard lumps with a specific radius in each case, and capable of impact. As a convenient form of words, there is no objection to this, though it cannot approximate to the truth. If we reason in terms of an æther, the electron and nucleus are both states of strain in the æther, in some sense complementary, and any constants, such as charges and radii, associated with them, must be, in fact, constants of the possible strains which the æther can retain permanently — and therefore constants of the æther itself. As regards the

radius of an electron, for example, if the strain outside its centre follows a highly convergent law with distance r , it must be of the type $f\left(\frac{r}{a}\right)$, where a is a length—and this is essentially the so-called radius of the electron, or the distance at which the strain-intensity has fallen to a specific small value. Such considerations were advanced by the author several years ago, and the universality of the constants of electrons and nuclei is thereby referred back to a universality of structure in an æther, on a scale so small that its effect is only felt in phenomena which we relate to a single electron or nucleus.

In such circumstances, interpenetration of electric charges merely means the coexistence of two separate strains at the same place. A double-mesh structure in the æther, with different line constants (radius of electron and nucleus) in its specification, would admit this possibility, so that two strain systems in the same region would not annihilate each other, and might move through each other. The analysis of this section indicates how such problems may be treated very simply, with a sufficient practical approximation.

We shall leave the problem of Pendulum-paths at this point, reserving the investigation of the more complex systems for a further paper.

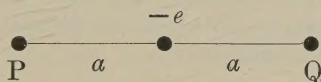
Nuclear Structure.

It is of interest to inquire into the implications inherent in the present view that nuclei have a structure built up from electrons and simpler nuclei—perhaps only the Hydrogen nucleus $+e$. This view is now practically general, and yet it is not without its difficulties. For if we consider even such simple systems of compound nuclei as, for example, a nucleus $2e$ and one electron, or the suggested Helium nucleus consisting of 4 Hydrogen nuclei and two electrons, it is very difficult to find an arrangement which restricts the total dimensions of the compound nucleus to any values comparable with the known dimensions.

It is almost unthinkable that the motions in these systems should not be subject to the quantizing principle, for their elements are “bound” in a still more intimate sense even than the external electrons of an atom. They can hardly be quantized by the introduction of a new quantum of action, different in order from h , and yet by the consideration of so simple a system as the suggested Helium atomic nucleus, it is easily seen that if the two electrons move in orbits in the

nucleus, the smallest possible orbits round the 4 Hydrogen nuclei are of atomic size. Either the law of force does, in fact, change—though experiments contradict this supposition—or the electrons are not in motion. The principle of coexistence already suggested may provide the only solution of these difficulties, but it is interesting to try, on more recognised lines, to obtain a nuclear representation.

We shall begin with a possible Hydrogen isotope—the so-called “inverted Bohr model” of Lenz, in which two nuclei rotate symmetrically round an electron. The structure seems very unstable, but the order of magnitude of the orbital radius must be the same as that in any more probable configuration, of this or of similar systems, in which the motion belongs to the nuclei.



If P and Q are the nuclei, $+e$, rotating with angular velocity ω in a circle of radius a ,

$$Ma^3\omega^2 = e^2(1 - \frac{1}{4}),$$

$$Ma^2\omega = \frac{\tau h}{2\pi},$$

whence the value of W is

$$W = \frac{2\pi^2 Me^4}{\tau^2 h^2} \cdot \frac{9}{16}.$$

If this system changed its quantum number, it would give radiations of the types— n being wave number,—

$$n = \frac{9}{16} \cdot \frac{M}{m} \cdot 109720 \left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2} \right),$$

which fall in the region of X-rays. Such nuclear specifications, in general, are suitable, as regards order of magnitude of emitted wave-lengths, for the representation of characteristic X-ray radiation, provided that the orbital motions are those of nuclei of mass M. This correspondence of theoretical and experimental magnitude does not appear to have been pointed out.

The radius of the nucleus is given, from the above equations, by

$$a = \frac{4}{3} \frac{\tau^2 h^2}{4\pi^2 M e^2}$$

and the angular velocity by

$$\omega = \frac{9}{16} \cdot \frac{8\pi^3 M e^4}{h^3 \tau^3}.$$

If a_H is the "normal" radius of a Hydrogen atom,

$$a/a_H = \frac{4}{3} \cdot \frac{m\tau^2}{M} = 0.0007 \tau^2.$$

For $\tau=1$, the smallest nucleus, this is almost comparable with the radius of an electron, and gives a nucleus which is not definitely too large, within experimental error.

The velocity of a nucleus is

$$a\omega = \frac{3\pi}{2} \cdot \frac{e^2}{h\tau},$$

which, with the usual values of e and h , becomes

$$a\omega = \frac{1.6}{\tau} \times 10^{-6},$$

which is quite small in comparison with the velocity of light.

The value of ω , compared with that of the electron in a normal Hydrogen atom, is given by

$$\omega/\omega_H = \frac{9}{16} \cdot \frac{M}{m\tau^3} = \frac{10^3}{\tau^2},$$

so that this configuration, in its influence on an outer orbital electron making the atom neutral, can be treated as at rest in some mean position.

We propose to compare the spectrum of this neutral atom, which should be an isotope of Hydrogen, with that of Hydrogen itself—not because the atom may be presumed to exist, but because the order of magnitude of the spectral difference is clearly that to be expected in light isotopes of any type dependent on a nucleus built up of electrons and Hydrogen nuclei. At present there is complete uncertainty, on the theoretical side, as to the spectral difference to be looked for in any isotopes.

Spectra of Isotopes.

There are two sources of difference between the spectra of two isotopic forms of the same element, (1) the effect of a different mass in the nucleus, and (2) the effect of the distribution of nuclear charge, which does not produce a field, in the neighbourhood of the electron whose states define the spectrum, of the form appropriate to the point charge which is the core of a simple Hydrogen atom. We shall consider the orders of magnitude of (1) and (2).

The fact that the Rydberg constant N occurs simply in all ordinary arc series spectra is a somewhat conclusive proof that such spectra are due to an electron which is not much disturbed by the motions of other electrons, so that the rest of the atom acts upon this electron, to a first approximation, after the manner of a Hydrogen nucleus. For if two electrons were moving in outer orbits of approximately equal dimensions, this constant would be changed, as is easily seen, to $N(2 - \frac{1}{4})^2$ in any good approximation to a spectral formula.

Consider an element of atomic weight M_σ —roughly σM_1 , where M_1 is the mass of a Hydrogen atom, for the mass is nearly all concentrated in the positive charges.

If one electron is more remote than the others, a series spectrum can be developed, in which the Rydberg constant is

$$N \frac{M_\sigma}{M_\sigma + m},$$

where m is the mass of an electron. This differs from the Hydrogen constant

$$N \frac{M_1}{M_1 + m}$$

by an amount roughly equal to

$$N \left\{ \frac{\sigma M_1}{\sigma M_1 + m} - \frac{M_1}{M_1 + m} \right\} = N \frac{(\sigma - 1)}{\sigma} \frac{m}{M_1}.$$

Let the element now have an isotope, also of the same atomic number but with $\sigma + 1$ positive charges and an electron in its nucleus. Then the difference between the Rydberg constants of the two isotopes is

$$N \left\{ \frac{\sigma M_1}{\sigma M_1 + m} - \frac{(\sigma + 1)M_1}{(\sigma + 1)M_1 + m} \right\} = - \frac{m}{M_1} \cdot \frac{1}{\sigma(\sigma + 1)} N$$

to a sufficient approximation.

The proportional change in wave-length is effectively, in passing from one isotope to the other,

$$\frac{1}{\sigma(\sigma+1)} \frac{m}{M_1} \lambda,$$

where λ is the wave-length of any line.

For example, in Lithium, $\sigma=6$, for the lighter isotope needs 6 Hydrogen nuclei, and for the line $\lambda 6708$, the possible change is

$$\frac{6708}{6 \times 7 \times 1835} \text{Å} = 0.087 \text{Å}.$$

But in an element like lead, where $\sigma=200$ roughly, the change is only, in the region $\lambda 5000$, about

$$\frac{5000}{200 \times 201 \times 1835} \text{Å} = 0.00006.$$

The change from this source thus diminishes very rapidly down the periodic table.

The changes of this type which occur among the various lines of the same series should be proportional to their wave-lengths, to a sufficient practical approximation, for the effect is merely an alteration in the Rydberg constant.

It is clear that the effect to be expected in the Lithium atom, though comparatively large, is not comparable with that found by McLennan recently and ascribed to isotopes. Other interpretations have been put forward. The effect in Lead, however, is comparable with that actually known to occur (Merton).

We now consider the effect of the second type, due to the fact that the field of the nucleus and inner electrons is not that of a single point charge. In the case of the Hydrogen isotope, founded above on the inverted Bohr model, the nuclear radius is $a = 7\tau^2 \times 10^{-13}$ cm. approximately, and the angular velocity is

$$\omega = \frac{10^3}{\tau^2} \omega_H,$$

where ω_H is the value in a normal Hydrogen atom. Clearly the nuclear period is very much smaller, and the nuclear field on an electron may be replaced by its average value over one of its periods.

In the plane of the nuclear motion, the potential at time t ,

at distance r , is, with the notation in the figure,

$$\begin{aligned} V &= -\frac{e}{r} + \frac{e}{r_1} + \frac{e}{r_2} \\ &= -\frac{e}{r} + \frac{e}{\sqrt{r^2 + a^2 + 2ar \cos(\theta - \omega t)}} \\ &\quad + \frac{e}{\sqrt{r^2 + a^2 - 2ar \cos(\theta - \omega t)}} \\ &= -\frac{e}{r} + \frac{e}{r} \sum_0^\infty \frac{a^{2n}}{r^{2n}} P_n \{\cos(\theta - \omega t)\} \{1 + (-1)^n\}. \end{aligned}$$

The mean value of any odd power of $\cos(\theta - \omega t)$ is zero. Thus

$$V = -\frac{e}{r} + \frac{2e}{r} \sum_0^\infty \frac{a^{2n}}{r^{2n}} P_{2n} \{\cos(\theta - \omega t)\},$$

which gives, as mean value to order a^2 ,

$$V = -\frac{e}{r} + \frac{2e}{r} \left\{ 1 + \frac{a^2}{4r^2} \right\},$$

the mean value of $\cos^2(\theta - \omega t)$ being $\frac{1}{2}$.

Thus

$$V = \frac{e}{r} + \frac{ea^2}{2r^3}.$$

Just as Bohr's simple theory with circular orbits gave the essentials of the Hydrogen spectrum, so, with the present law of potential, the supposition of circular orbits saves much analysis and gives the main spectrum of the outer electron. If it moves in a circle of radius b with angular velocity ω ,

$$mb\omega^2 = e^2 \left(\frac{1}{b^2} + \frac{3}{2} \frac{a^2}{b^4} \right),$$

$$mb^2\omega = \frac{nh}{2\pi},$$

whence

$$b\omega = \frac{2\pi e^2}{nh} \left(1 + \frac{3}{2} \frac{a^2}{b^2} \right),$$

$$b = \frac{n^2 h^2}{4\pi^2 m e^2}$$

to the first order, and

$$W = \frac{2\pi^2 m e^4}{n^2 h^2} \left(1 + \frac{3a^2}{b^2} \right).$$

The Rydberg constant is changed by the fraction $3a^2/b^2$ of itself for the case $n=1$, and this is the greatest change, due to non-localization of the nuclear charge. With $b=5 \cdot 10^{-9}$, $a/b=0\cdot0007 \tau^2$, the change $\delta\lambda$ in a wave-length λ is given by

$$\frac{\delta\lambda}{\lambda} = 0\cdot0^5149 \tau^2,$$

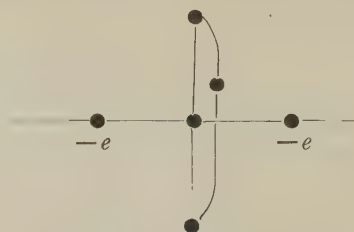
and for H_α , it would be

$$\delta\lambda = 0\cdot0098 \tau^2 \text{ \AA},$$

which could be detected if the isotope existed. The interest of the investigation lies, however, in the fact that this is the order of magnitude to be expected in isotopes of light atoms generally—and it is small in comparison with the other effect. The effect to be expected for Lithium is therefore of the order already specified.

More complex Nuclei.

The Helium nucleus now usually suggested consists of four Hydrogen nuclei or protons, and two electrons. The only simple arrangement they appear to admit, with the motion belonging only to nuclei, is shown in the figure.



The nuclei are equally spaced in a circular orbit, the electrons being on the axis. If $2a$ is the distance between the electrons, and b the radius of the orbit, we have

$$\frac{e^2}{4a^2} = \frac{4e^2a}{(a^2+b^2)^{3/2}},$$

$$Mb^3\omega^2 = b^2 \left\{ \frac{2e^2b}{(a^2+b^2)^{3/2}} - \frac{e^2}{b^2} \cdot \frac{1}{4} S_4 \right\},$$

where

$$S_4 = \operatorname{cosec} \frac{\pi}{4} + \operatorname{cosec} \frac{\pi}{2} + \operatorname{cosec} \frac{3\pi}{4} = 1 + 2\sqrt{2}.$$

Thus

$$b = a \sqrt{2^{8/3} - 1}, \quad \sqrt{a^2 + b^2} = 2^{4/3}a,$$

$$Mb^3\omega^2 = e^2 \left\{ \frac{2^{8/3} - 1}{8} - \frac{1}{4} - \frac{1}{\sqrt{2}} \right\}$$

$$= 0.178 e^2.$$

With a quantum of angular momentum at least for each nucleus,

$$Mb^2\omega = \frac{\tau\hbar}{2\pi}.$$

Thus

$$b\omega = 0.178 \frac{2\pi e^2}{\tau\hbar},$$

$$b = \frac{1}{0.178} \frac{\tau^2\hbar^2}{4\pi^2 M e^2},$$

and thence

$$a = \frac{(2^{8/3} - 1)^{-1/2}}{0.178} \frac{\tau^2\hbar^2}{4\pi^2 M e^2},$$

while the angular velocity is again so large that any external electron moves effectively in the "mean field" of the nucleus.

If a_H is again the normal radius of a Hydrogen atom, we find

$$\frac{a}{a_H} = 2.43 \frac{m}{M} \tau^2,$$

$$\frac{b}{a_H} = 5.62 \frac{m}{M} \tau^2.$$

The field of this nucleus, at a point on its axis, distant z from the centre, is

$$V = -\frac{e}{z+a} - \frac{e}{z-a} + \frac{4e}{\sqrt{z^2 + b^2}},$$

or, at a sufficient distance, compared with a or b ,

$$V = \frac{2e}{z} - \frac{2e}{z^3} (a^2 + b^2),$$

which, at any point (r, θ) in spherical polars, generalizes to

$$V = \frac{2e}{r} - \frac{2e}{r^3} (a^2 + b^2) \left(\frac{3 \cos^2 \theta - 1}{2} \right)$$

as the mean field of the nucleus.

This law of force does not admit a strictly circular orbit, but the occurrence of approximately circular orbits is possibly due to the smallness of the last term of V. If an approximate orbit is $r=c$, we may replace, for a sufficient first approximation, the last term by its mean value, thus writing

$$r = c, \quad \cos^2 \theta = \frac{1}{2}.$$

The equation of energy then becomes

$$\frac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2) - \frac{2e^2}{r} - \frac{2e^2}{c^3} \frac{(a^2 + b^2)}{4} = -W,$$

or

$$\frac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2) - \frac{2e^2}{r} = -W_1,$$

where $W_1 = W + \frac{2e^2}{4c^3}(a^2 + b^2)$.

This can be quantized in the ordinary way, the result being known to be

$$W_1 = \frac{8\pi^2 m e^4}{n^2 \hbar^2},$$

where n is an integer. Moreover, for nucleus $2e$, the radius c becomes

$$c = \frac{n^2 \hbar^2}{4\pi^2 m e^2}.$$

to its first approximation, or mean value.

Accordingly,

$$\begin{aligned} W &= W_1 - \frac{2e^2}{4c^3}(a^2 + b^2) \\ &= \frac{8\pi^2 m e^4}{n^2 \hbar^2} - \frac{8\pi^2 m e^4}{n^2 \hbar^2} \cdot \frac{a^2 + b^2}{4c^2}. \end{aligned}$$

The proportional change in W due to nuclear distribution is therefore $(a^2 + b^2)/4c^2$, and the corresponding change in any wave-length λ is given by

$$\frac{\delta\lambda}{\lambda} = \frac{a^2 + b^2}{4c^2},$$

due to change in its series limit.

If τ is the nuclear quantum number, by preceding results,

$$\frac{a}{a_H} = 2.43 \frac{m}{M} \tau^2, \quad \frac{b}{a_H} = 5.62 \frac{m}{M} \tau^2,$$

and c is the radius of the Helium atom with a double charge.

The normal value of this radius, corresponding to $n=1$, is $\frac{1}{4}$ that of the Hydrogen atom (a_H). For a quantum number n , the radius is proportional to n^2 . Thus the proportional change in the Helium line of wave number

$$4N \left\{ \frac{1}{p^2} - \frac{1}{q^2} \right\}$$

is

$$\frac{\delta\lambda}{\lambda} = 4 \{ (2.43)^2 + (5.62)^2 \} \left(\frac{m}{M} \right)^2 \tau^4 \left(\frac{1}{p^2} - \frac{1}{q^2} \right),$$

and, curiously, becomes proportional to λ^{-1} , so that $\delta\lambda$ is constant.

We find, on reduction,

$$\frac{\delta\lambda}{\lambda} = 0.0427 \tau^2 \left(\frac{1}{p^2} - \frac{1}{q^2} \right).$$

For example, the line $\lambda 4686$, for which $p=2$, $q=3$, gives

$$\begin{aligned} \delta\lambda &= 0.0427 \tau^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) 4686 \\ &= 0.018 \tau^2 \end{aligned}$$

in Ångström units. The probable value of τ is unity, so that the change does not appreciably affect Fowler's calculation of m/M by comparison of the spectra of Hydrogen and of charged Helium.

But the correction for ionized Helium is much greater than for Hydrogen, and clearly it tends to increase as the atomic number of the element increases—so long as that atomic number is made up, in the nucleus, of a preponderance of protons or charged Hydrogen nuclei. It will clearly be very difficult to make up yet more complex nuclei in this way, with the experimental restrictions as to their dimensions, and as to the available law of force among their elements is concerned.

The general conclusion of this section, while not decisive, is certainly adverse to the hypothesis of nuclei made up entirely from Hydrogen. Perhaps our supposition that nuclear motions are subject to the quantizing relation is incorrect, though it is difficult to imagine, or to have faith in, any alternative.

We shall leave the matter at this point, with a view to a further communication.

December 27, 1922.

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LXXXII. *Some Approximations to Hypergeometric Functions.*
 By DOROTHY M. WRINCH, D.Sc., *Fellow of Girton College,*
Cambridge, and Member of the Research Staff, University
College, London.*

THE importance of the Bessel functions

$$J_n(x) = \frac{(x/2)^n}{\Gamma(1+n)} \left\{ 1 - \frac{(x/2)^2}{1!(1+n)} + \frac{(x/2)^4}{2!(1+n)(2+n)} - \dots \right\}$$

$$I_n(x) = \frac{(x/2)^n}{\Gamma(1+n)} \left\{ 1 + \frac{(x/2)^2}{1!(1+n)} + \frac{(x/2)^4}{2!(1+n)(2+n)} + \dots \right\}$$

in mathematical physics has long been recognized. These functions are, however, particular cases of the hypergeometric function with s denominators †, which may be defined by the power series

$$1 + \frac{z}{1!(1+b_1)(1+b_2)\dots(1+b_{s-1})} + \frac{z^2}{2!(1+b_1)(2+b_1)(1+b_2)(2+b_2)\dots(1+b_{s-1})(2+b_{s-1})} + \dots$$

In the present paper, we are concerned with the hypergeometric function with four denominators

$$1 + \frac{z}{1!(1+b_1)(1+b_2)(1+b_3)} + \frac{z^2}{2!(1+b_1)(2+b_1)(1+b_2)(2+b_2)(1+b_3)(2+b_3)} + \dots, \quad (1)$$

when z is real and positive and when z is real and negative, and, further, with the hypergeometric function with five denominators and one numerator,

$$1 + \frac{(1+a)z}{1!(1+b_1)(1+b_2)(1+b_3)(1+b_4)} + \frac{(1+a)(2+a)z^2}{2!(1+b_1)(2+b_1)(1+b_2)(2+b_2)(1+b_3)(2+b_3)(1+b_4)(2+b_4)} + \dots, \quad (2)$$

when z is real and positive and when z is real and negative.

* Communicated by the Author.

† Alternative methods of definition and certain properties of these functions are given in a forthcoming paper by the present writer.

The function (2) is evidently a particular case of the hypergeometric function with s denominators and t numerators,

$$1 + \frac{(1+a_1)(1+a_2)\dots(1+a_t)z}{1!(1+b_1)(1+b_2)\dots(1+b_s)} \\ + \frac{(1+a_1)(2+a_1)\dots(1+a_t)(2+a_t)z^2}{2!(1+b_1)(2+b_1)\dots(1+b_s)(2+b_s)} + \dots$$

The functions (1) and (2) have recently occurred in the problem of the lateral vibrations of bars of non-uniform cross-section*. In this problem the displacement is given in terms of the function

$$1 + \frac{x}{1!(1+b_1)(1+b_2)(1+b_3)} \\ + \frac{x^2}{2!(1+b_1)(2+b_1)(1+b_2)(2+b_2)(1+b_3)(2+b_3)} + \dots,$$

and the period equation takes the form

$$1 - \frac{(1+a)x}{1!(1+b_1)(1+b_2)(1+b_3)(1+b_4)} \\ + \frac{(1+a)(2+a)x^2}{2!(1+b_1)(2+b_1)\dots(1+b_4)(2+b_4)} - \dots = 0. \quad (3)$$

The present paper contains a simple approximation to the value of the functions (1), (2), when z is large and real and positive or large and real and negative, and an expression which gives to a high degree of accuracy the roots of the equation (3).

1.

1.1. It is known that for values of x which are real and positive, the asymptotic expansion for large values of x of the series

$$y_1 = \frac{1}{\Gamma(1+b_1)\Gamma(1+b_2)\Gamma(1+b_3)} \\ \left\{ 1 + \frac{(x/4)^4}{1!(1+b_1)(1+b_2)(1+b_3)} \right. \\ \left. + \frac{(x/4)^8}{2!(1+b_1)(2+b_1)(1+b_2)(2+b_2)(1+b_3)(2+b_3)} + \dots \right\}$$

* Cf. a paper by the present writer in the Proceedings of the Royal Society, A. vol. 101 (1922).

is given by

$$y_1 = \frac{e^x(x/4)^{-\sigma}}{2(2\pi)^{3/2}} \left\{ 1 + \frac{\alpha_1}{x} + \frac{\alpha_2}{x^2} + O\left(\frac{1}{x^3}\right) \right\},$$

where

$$\sigma = b_1 + b_2 + b_3 + 3/2$$

and α_1 and α_2 are certain functions of b_1 , b_2 , and b_3 . Further, the series

$$y_2 = \frac{\Gamma(1+\gamma)}{\Gamma(1+b_1)\Gamma(1+b_2)\Gamma(1+b_3)\Gamma(1+b_4)} \left\{ 1 + \frac{(1+\gamma)(x/4)^4}{1!(1+b_1)(1+b_2)(1+b_3)(1+b_4)} + \dots \right\},$$

which reduces to y_1 in the special case when $\gamma = b_4$, has the asymptotic expansion

$$y_2 = \frac{e^x(x/4)^{-\tau}}{2(2\pi)^{3/2}} \left\{ 1 + \frac{\delta_1}{x} + \frac{\delta_2}{x^2} + O\left(\frac{1}{x^3}\right) \right\},$$

when x is real, positive, and large. In this expression

$$\tau = b_1 + b_2 + b_3 + b_4 - \gamma + 3/2$$

and δ_1 , δ_2 are certain functions of b_1 , b_2 , b_3 , b_4 , and γ .

1.2. To find the values of δ_1 , δ_2 , which will, of course, yield the values of α_1 , α_2 if b_4 be put equal to γ , we remark that y_2 satisfies the linear differential equation of the fifth order

$$\mathfrak{D}(\mathfrak{D}+4b_1)(\mathfrak{D}+4b_2)(\mathfrak{D}+4b_3)(\mathfrak{D}+4b_4)y_2 = x^4(\mathfrak{D}+4+4\gamma)y_2.$$

If

$$y_2 = e^x x^{-\tau} y,$$

it follows that

$$\mathfrak{D}y_2 = e^x x^{-\tau} (\mathfrak{D} + x - \tau)y,$$

and the equation for y consequently becomes

$$(x - \beta_1 + \mathfrak{D})(x - \beta_2 + \mathfrak{D})(x - \beta_3 + \mathfrak{D})(x - \beta_4 + \mathfrak{D})(x - \beta_5 + \mathfrak{D})y = x^4(x - \sigma + 4 + 4\gamma + \mathfrak{D})y,$$

if we write

$$\beta_r = -\tau + 4b_r, \quad (r=1, 2, 3, 4),$$

$$\beta_5 = -\tau.$$

The left side of this equation is evidently of the form

$$y(x^5 + {}_1a_1x^4 + {}_1a_2x^3 + \dots) + \mathfrak{D}y(5x^4 + {}_2a_1x^3 + {}_2a_2x^2 + \dots) + \mathfrak{D}^2y(10x^2 + \dots) + \mathfrak{D}^3y(10x^2 + \dots) + \mathfrak{D}^4y(5x + \dots) + \mathfrak{D}^5y.$$

Now consider the expression

$$\prod_{r=1}^n (x - \beta_r + \mathfrak{S})y;$$

it is evidently of the form

$$y(x^n + {}_1a_1x^{n-1} + {}_1a_2x^{n-2} + \dots) + \mathfrak{S}y(nx^{n-1} + {}_2a_1x^{n-2} + \dots) + \dots + \mathfrak{S}^ny.$$

We can obtain by induction the value of the $({}_ra_s)$ coefficients. In particular,

$$\begin{aligned} {}_1a_2 &= \Sigma_2 + \frac{(n-1)(n-2)}{2} \Sigma_1 + \frac{n(n-1)(n-2)(3n-5)}{24}, \\ {}_1a_3 &= \Sigma_3 + \frac{(n-2)(n-3)}{2} \Sigma_2 + \frac{(n-1)(n-2)(n-3)(3n-8)}{24} \Sigma_1 \\ &\quad + \sum_{s=1}^n \frac{(s-1)(s-2)(s-3)^2(3s-8)}{24}, \end{aligned}$$

where Σ_r represents the products r at a time of the n quantities $\beta_1, \beta_2, \dots, \beta_n$. In the particular case under discussion, $n=5$, and we have

$$\begin{aligned} {}_1a_2 &= \Sigma_2 + 6\Sigma_1 + 25, \\ {}_1a_3 &= \Sigma_3 + 3\Sigma_2 + 7\Sigma_1 + 15, \\ {}_2a_2 &= 4\Sigma_1 + 30, \end{aligned}$$

where Σ_r represents the sum of the products r at a time of the five quantities

$$-\tau + 4b_1, \quad -\tau + 4b_2, \quad -\tau + 4b_3, \quad -\tau + 4b_4, \quad -\tau.$$

1.3. The equation for y may conveniently be written in the form

$$\begin{aligned} y\{({}_1a_1 - 4 + 4\gamma - \tau)x^4 + {}_1a_2x^3 + \dots\} \\ + \mathfrak{S}y\{4x^4 + {}_2a_1x^3 \dots\} + \dots = 0. \end{aligned}$$

Solving for y in series, we may put

$$y = 1 + \frac{\delta_1}{x} + \frac{\delta_2}{x^2} + \dots$$

Equating to zero the coefficient of the term of highest power in x , namely, x^4 , we obtain the result

$${}_1a_1 - (4 + 4\gamma - \tau) = 0.$$

The equation for y is now

$$y({}_1a_2x^2 + {}_1a_3x^3 + \dots) + {}_2y(4x^3 + {}_2a_2x^2 + \dots) + \dots = 0,$$

and equating to zero the terms in x^3 , x^2 , and so on, we get the series of equations

$$\begin{aligned} {}_1a_2 - 4\delta_1 &= 0, \\ {}_1a_3 + \delta_1 \cdot {}_1a_2 + 8\delta_2 - \delta_2 \cdot {}_2a_2 &= 0, \\ &\dots\dots\dots \end{aligned}$$

yielding the results

$$\begin{aligned} \delta_1 &= \frac{{}_1a_2}{4} = \frac{1}{4}(\Sigma_2 + 6\Sigma_1 + 25), \\ 8\delta_2 &= \delta_1({}_2a_2 - {}_1a_2) - {}_1a_3, \\ &= -\delta_1(\Sigma_2 + 2\Sigma_1 - 20) - (\Sigma_3 + 3\Sigma_2 + 7\Sigma_1 + 15). \end{aligned}$$

Succeeding equations will yield the value of the succeeding coefficients $\delta_3, \delta_4, \dots$. With the values of δ_1, δ_2 obtained above, we therefore have the approximation to the value of y_2 in the form

$$y_2 = \frac{e^x}{2(2\pi)^{3/2}} \left(\frac{x}{4}\right)^{-\tau} \left\{ 1 + \frac{\delta_1}{x} + \frac{\delta_2}{x^2} + O\left(\frac{1}{x^3}\right) \right\}.$$

1.4. We may write down a similar result for the function y_1 .

$$y_1 = \frac{e^x(x/4)^{-\sigma}}{2(2\pi)^{3/2}} \left\{ 1 + \frac{\alpha_1}{x} + \frac{\alpha_2}{x^2} + O\left(\frac{1}{x^3}\right) \right\},$$

where

$$\begin{aligned} \sigma &= b_1 + b_2 + b_3 + 3/2, \\ \alpha_1 &= \frac{1}{4}(\Sigma_2' + 3\Sigma_1' + 7), \\ 8\alpha_2 &= -\alpha_1(\Sigma_2' + 1) + \Sigma_3' + \Sigma_2' + \Sigma_1' + 1, \end{aligned}$$

Σ_r' representing the sum of the products r at a time of the four quantities

$$4b_1 - \sigma, \quad 4b_2 - \sigma, \quad 4b_3 - \sigma, \quad -\sigma^*.$$

This result may be obtained *ab initio* by obtaining the differential equation for y where

$$y_1 = e^x x^{-\sigma} y$$

* For convenience in actual computation, it may be remarked that $\Sigma_1' = 6$, in virtue of the relation between σ and b_1, b_2, b_3 .

and solving in a series

$$y = 1 + \frac{\alpha_1}{x} + \frac{\alpha_2}{x^2} + \dots,$$

or, more conveniently, by writing $b_4 = \gamma$ in the result obtained above for the series y_2 .

1.5. The series

$$y_3 = \frac{1}{\Gamma(1+b_1)\Gamma(1+b_2)\Gamma(1+b_3)} \\ \left\{ 1 - \frac{(x/4)^4}{1!(1+b_1)(1+b_2)(1+b_3)} \right. \\ \left. + \frac{(x/4)^8}{2!(1+b_1)(2+b_1)(1+b_2)(2+b_2)(1+b_3)(2+b_3)} - \dots \right\}$$

$$y_4 = \frac{\Gamma(1+\gamma)}{\Gamma(1+b_1)\Gamma(1+b_2)\Gamma(1+b_3)\Gamma(1+b_4)} \\ \left\{ 1 - \frac{(1+\gamma)(x/4)^4}{1!(1+b_1)(1+b_2)(1+b_3)(1+b_4)} \right. \\ \left. + \frac{(1+\gamma)(2+\gamma)(x/4)^8}{2!(1+b_1)(2+b_1)(1+b_2)(2+b_2)(1+b_3)(2+b_3)(1+b_4)(2+b_4)} - \dots \right\}$$

may be treated on similar lines. We will deal first with the series y_4 . Now, if x is real, positive, and large,

$$y_4 = \frac{e^{\frac{x \cos \frac{\pi}{4}}{4}} (x/4)^{-\tau}}{(2\pi)^{3/2}} \left\{ \cos \left(x \sin \frac{\pi}{4} - \frac{\pi\tau}{4} \right) \right. \\ \left. + \frac{\delta_1}{x} \cos \left(x \sin \frac{\pi}{4} - \frac{\pi(\tau+1)}{4} \right) \right. \\ \left. + \frac{\delta_2}{x^2} \cos \left(x \sin \frac{\pi}{4} - \frac{\pi(\tau+2)}{4} \right) + O\left(\frac{1}{x^3}\right) \right\},$$

where, as before,

$$\tau = b_1 + b_2 + b_3 + b_4 - \gamma + 3/2,$$

$$\delta_1 = \frac{1}{4}(\Sigma_2 + 6\Sigma_1 + 25),$$

$$8\delta_2 = -\delta_1(\Sigma_2 + 2\Sigma_1 - 20) - (\Sigma_3 + 3\Sigma_2 + 7\Sigma_1 + 15)$$

Similarly,

$$y_3 = \frac{e^{x \cos \frac{\pi}{4} (x/4)^{-\sigma}}}{(2\pi)^{3/2}} \left\{ \cos \left(x \sin \frac{\pi}{4} - \frac{\pi \sigma}{4} \right) \right. \\ \left. + \frac{\alpha_1}{x} \cos \left(x \sin \frac{\pi}{4} - \frac{\pi(\sigma+1)}{4} \right) \right. \\ \left. + \frac{\alpha_2}{x^2} \cos \left(x \sin \frac{\pi}{4} - \frac{\pi(\sigma+2)}{4} \right) + O\left(\frac{1}{x^3}\right) \right\}$$

and

$$\sigma = b_1 + b_2 + b_3 + 3/2,$$

$$\alpha_1 = \frac{1}{4}(\Sigma_2' + 3\Sigma_1' + 7),$$

$$8\alpha_2 = -\alpha_1(\Sigma_2' + 1) + (\Sigma_3' + \Sigma_2' + \Sigma_1' + 1).$$

The results given above enable us to estimate the value of y_1, y_2, y_3 , and y_4 in a simple manner, by the calculation of the coefficients $\alpha_1, \alpha_2, \delta_1, \delta_2$. The error in adopting these approximations is of relative order $\frac{1}{x^3}$, which is sufficient in the case of many practical applications.

2.

2.1. In order to obtain an approximation to the roots of an equation of the type

$$y_4 = 0,$$

we may adopt the approximation to the value of y_4 when x is large, which was obtained above. We therefore consider the roots of the equation

$$\cos \left(x \sin \frac{\pi}{4} - \frac{\pi \tau}{4} \right) + \frac{\alpha_1}{x} \cos \left(x \sin \frac{\pi}{4} - \frac{\pi(\tau+1)}{4} \right) \\ + \frac{\alpha_2}{x^2} \cos \left(x \sin \frac{\pi}{4} - \frac{\pi(\tau+2)}{4} \right) = 0.$$

If we put

$$\frac{\pi \tau}{4} + (s - \frac{1}{2})\pi = \lambda_s,$$

we may write the equation

$$\sin\left(x \sin \frac{\pi}{4} - \lambda_s\right) + \frac{\alpha_1}{x} \sin\left(x \sin \frac{\pi}{4} - \lambda_s - \frac{\pi}{4}\right) + \frac{\alpha_2}{x} \sin\left(x \sin \frac{\pi}{4} - \lambda_s - \frac{\pi}{2}\right) = 0.$$

A first approximation when x is large is evidently

$$x \sin \frac{\pi}{4} = \lambda_s.$$

Then, putting

$$x \sin \frac{\pi}{4} - \lambda_s = \epsilon_s,$$

the equation is

$$\sin \epsilon_s + \frac{\alpha_1}{x} \sin\left(\epsilon_s - \frac{\pi}{4}\right) + \frac{\alpha_2}{x^2} \sin\left(\epsilon_s - \frac{\pi}{2}\right) = 0,$$

and we obtain the result

$$\left(1 + \frac{\alpha_1}{x\sqrt{2}}\right) \sin \epsilon_s = \left(\frac{\alpha_1}{x\sqrt{2}} + \frac{\alpha_2}{x^2}\right) \cos \epsilon_s.$$

If $1/\lambda_s^3$ and ϵ_s^3 be neglected, this becomes

$$\left(1 + \frac{\alpha_1}{2(\lambda_s + \epsilon_s)}\right) \sin \epsilon_s = \left(\frac{\alpha_1}{2(\lambda_s + \epsilon_s)} - \frac{\alpha_2}{2(\lambda_s + \epsilon_s)^2}\right) \cos \epsilon_s,$$

which yields the result

$$\epsilon_s = \frac{\alpha_1}{2\lambda_s} - \frac{\alpha_1^2}{4\lambda_s^2} - \frac{\alpha_2}{2\lambda_s^2}.$$

Thus, to the order $1/\lambda_s^2$, the roots of the equation $y_4=0$ are given by

$$x \sin \frac{\pi}{4} = \lambda_s + \frac{\alpha_1}{2\lambda_s} - \frac{\alpha_1^2 + 2\alpha_2}{4\lambda_s^2},$$

with

$$\lambda_s = \frac{\pi\tau}{4} + (s - \frac{1}{2})\pi.$$

2.2. We may calculate the roots given by this approximation in a particular case. Let

$$y_4 = \frac{1}{\Gamma 3 \Gamma \frac{3}{2} \Gamma 4} \left\{ 1 - \frac{(x/2)^4}{2 \cdot 4 \cdot 5 \cdot 6} + \frac{(x/2)^8}{2 \cdot 4 \cdot 5 \cdot 6 \cdot 4 \cdot 6 \cdot 7 \cdot 8 \cdots} \right\} :$$

it is known that this series is a multiple of the function

$$\left\{ J_2 \left(x \sin \frac{\pi}{4} \right) I_3 \left(x \sin \frac{\pi}{4} \right) + I_2 \left(x \sin \frac{\pi}{4} \right) J_3 \left(x \sin \frac{\pi}{4} \right) \right\} / x^5,$$

where J_2, J_3, I_2, I_3 are Bessel functions.

The roots of the equation

$$y_4 = 0$$

are then given by the approximation

$$x \sin \frac{\pi}{4} = \lambda_s + \frac{\alpha_1}{2\lambda_s}$$

to the order $1/\lambda_s^2$, where

$$\tau = b_1 + b_2 + b_3 + b_4 - \gamma = 3/2,$$

$$\lambda_s = \frac{\pi}{4} \tau + (s - \frac{1}{2})\pi,$$

the values of the parameters being in this case given by

$$b_1, b_2, b_3 = 1, 3/2, 2 : b_4 = \gamma.$$

Thus, in this case

$$\tau = 6, \quad \lambda_s = (s + 1)\pi.$$

Further,

$$\Sigma_1 = -10, \quad \Sigma_2 = 20,$$

so that

$$\alpha_1 = \frac{1}{4}(\Sigma_2 + 6\Sigma_1 + 25) = -\frac{15}{4}.$$

Therefore, neglecting terms of order $1/\lambda_s^2$, we have

$$x \sin \frac{\pi}{4} = (s + 1)\pi - \frac{15}{8\pi(s + 1)}.$$

The first nine roots of the equation

$$J_2(y) I_3(y) + I_2(y) J_3(y) = 0$$

are known. The values of y which satisfy this equation are

evidently the values of $x \sin \frac{\pi}{4}$, which satisfy the equation

$y_4 = 0$ in this particular case. Thus, the fact that the first nine roots are known offers a way of testing the approxima-

tion for the values of $x \sin \frac{\pi}{4}$ which satisfy the equation

$y_4 = 0$ which has been given above. We exhibit the two sets of values in the appended table.

FIG. 1.

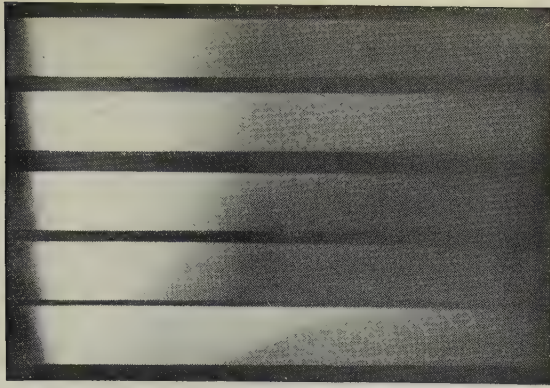


FIG. 2.

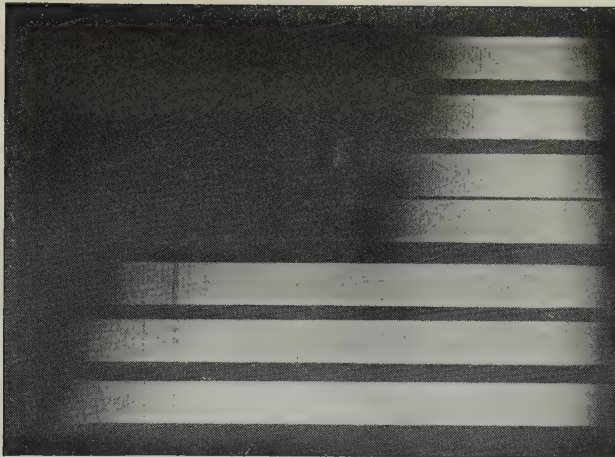


FIG. 3.

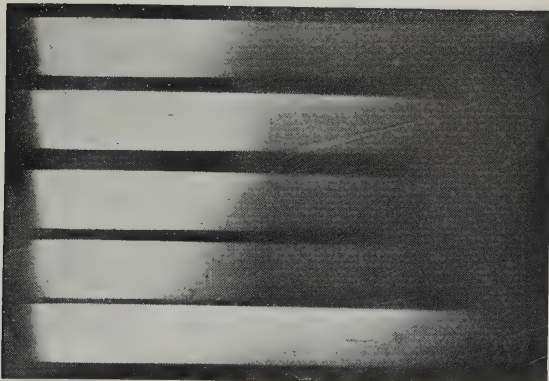


FIG. 4.

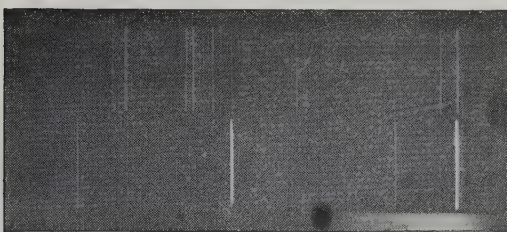


FIG. 5.

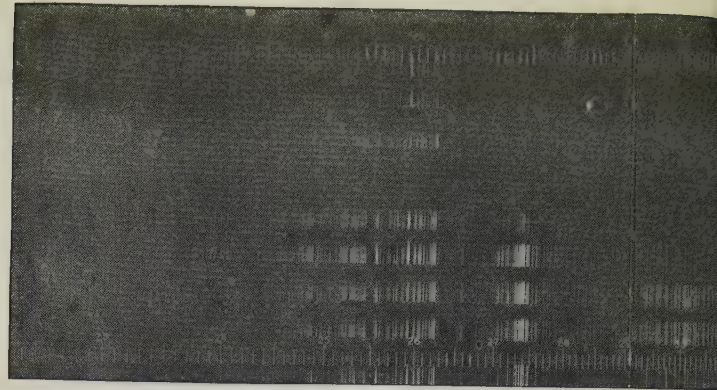


FIG. 6.

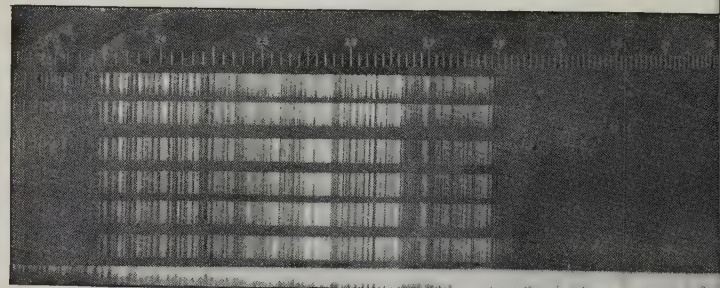


FIG. 7.

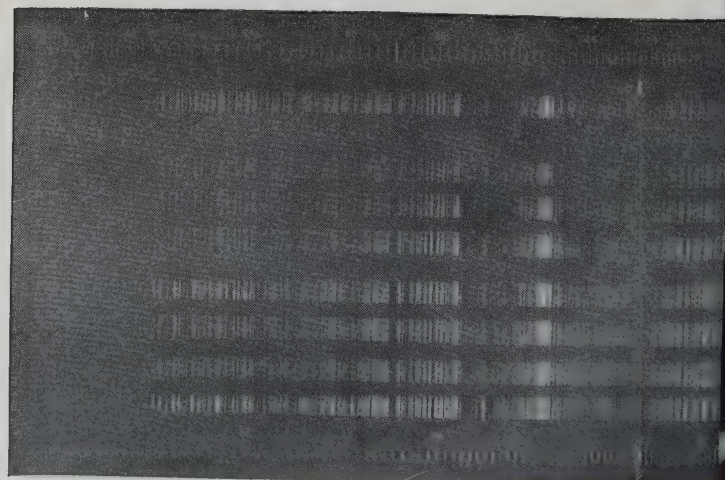


FIG. 8.

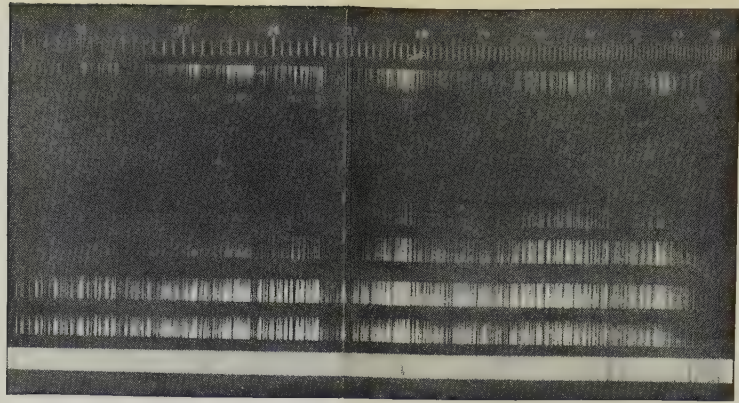


FIG. 9.

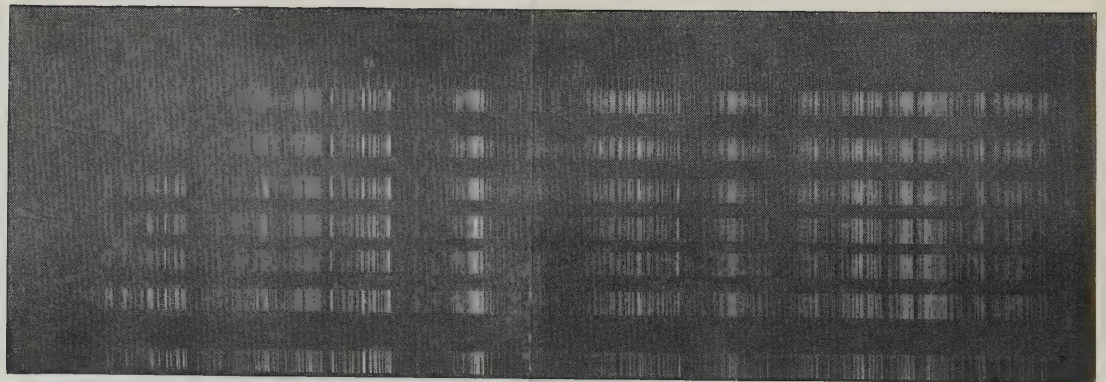
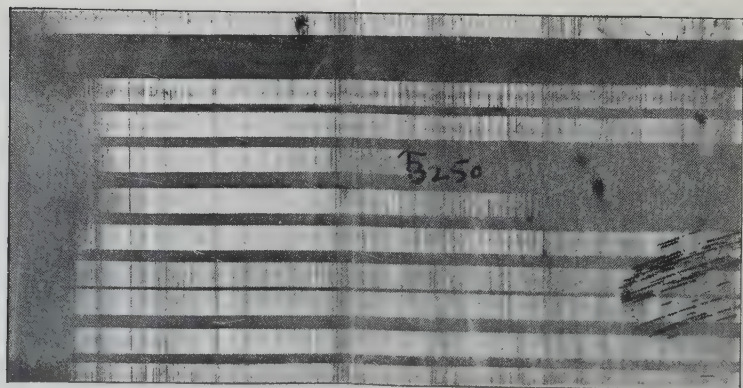


FIG. 10.



$$x \sin \frac{\pi}{4}.$$

s.	Exact Value*.	Approximation.	Difference.
1	1.8807	1.9050	.0143
2	2.9275	2.9367	.0092
3	3.9478	3.9525	.0047
4	4.9591	4.9620	.0029
5	5.9660	5.9683	.0023
6	6.9714	6.9729	.0015
7	7.9751	7.9763	.0012
8	8.9781	8.9789	.0008
9	9.9804	9.9810	.0006

It appears, then, that the first two terms of the approximation give all the roots ($s=1, 2 \dots$) with an error of less than 2 per cent., and all the roots after the ninth with an error of less than .06 per cent.

LXXXIII. *Emission and Absorption of Halogens in the Visible and Ultra-violet Regions.* By A. L. NARAYAN, M.A., A.Inst.P., and D. GUNNAYYA, B.A.†

[Plate XI.]

COLOURED gases and vapours are remarkable for the complexity of the banded spectra they give by absorption at low temperatures. Of these, the absorption exerted by the halogens is specially interesting, as their emission and absorption spectra are not complementary. The subject was studied by Hasselberg, Morre, Liveing and Dewar, Friederichs, &c., more recent work on the subject being by Evans on the absorption of Bromine and Iodine at different temperatures (*Astrophysical Journal*, xxxii. p. 1, 1910), and by M. Kimura and M. Fukuda (*Science Abstracts*, Section A, p. 436, 1921) on the emission of Chlorine.

The following experiments were therefore undertaken with the object of studying the emission and absorption spectra of these vapours in the visible and ultra-violet, and the effect of pressure on the absorption.

* Cf. J. R. Airey, *Proceedings of the Physical Society of London*, vol. xxii. p. 227 (1911).

† Communicated by the Authors.

Before the Mathematics and Physics Section of the Indian Science Congress, held in Madras recently, the authors read a paper containing some of these experiments. This paper contains a full account of those and other experiments we have since performed on these vapours.

The methods employed in this work for studying the effect of pressure on absorption are similar to those adopted by H. Jones and Anderson in their extensive investigations on the absorption spectra of solutions, viz. (1) to keep the pressure of the vapour constant and to vary the depth of the absorption cell; (2) to keep the depth constant and vary the pressure, *i. e.* concentration; (3) to vary both, thickness and pressure, of the absorbing layer in such a way that their product remains the same.

For absorption in the visible region, a Hilger glass spectrograph with a constant-deviation prism is used, eye observations being made with a Hilger direct-vision spectroscope. For work in the ultra-violet region, a Hilger quartz spectrograph provided with a wave-length scale is used, in which the whole region from 0.2μ to 0.78μ can be obtained in one exposure on a plate 10 inches long. In all these cases the absorption cells are glass tubes of different lengths furnished with two side tubulures against the ends, and the ends are closed with plane plates of glass or quartz by means of sealing-wax. In the case of bromine and iodine, tubes of 20 to 25 cm. in length were used, but in the case of chlorine, as the selective absorption in the yellowish-green region could not be seen with the above length, we had to use tubes of about a metre in length.

In photographing the spectra, Schumann plates made by Adam Hilger, London, and Wratten & Wainwright panchromatic "A" were used.

Source of Light.—For work in the visible region we used in some experiments a carbon arc, and in some others sunlight, as in this case the Fraunhofer lines serve as reference lines; and for work in the ultra-violet we used iron arc with some inductance and resistance in series, as the spectrum of iron is very rich in ultra-violet radiations, and the lines in the ultra-violet are so closely set that they almost form a continuous spectrum.

The emission spectra were examined both by Geissler tubes and by special discharge-tubes of about 20 to 30 cm. in length, 1 to 1.5 cm. in diameter, and furnished with two side tubes containing freshly prepared pure and well-dried silver halides, just sufficient to cover the platinum electrodes sealed through the tubes, the discharge-tube being connected

by means of a side tubulure to an exhaustion pump; and for discharge a 10-inch Apps induction-coil with an electrolytic interruptor and a condenser in parallel was used.

The emission spectra of bromine and chlorine are line spectra, the nature of which depends on the intensity of discharge and the temperature of the tube. As the intensity was increased, some lines were reinforced and others disappeared. As can be seen from fig. 4 (Pl. XI.), showing the emission spectrum of bromine in the visible region, it is not the strongest lines that are reinforced and that persist in the spectrum when the discharge is increased. The same was found to be the case with chlorine.

When we were investigating absorption of light by these vapours at low temperatures, there appeared the work of Sir J. J. Dobbie and J. J. Fox in the Science Abstracts, who studied the absorption of light by these gases at temperatures from 20 to 1350°C. As they used a Nernst filament lamp as the source of light, it was not possible for them to go beyond 3100 A.U.; and we thought it desirable to continue our experiments to study the absorption at different temperatures by using the iron arc as the source of light, as it would take us to 2000 A.U., which can be conveniently examined by the quartz spectrograph we used in the first series of experiments; and as will be seen from the photographs of the absorption spectra, this has led us to some interesting results.

Absorption Spectra.—All these vapours give a banded spectrum in the yellowish-green region between 5800 and 5000 A.U., the bands being sharp on the violet side and fading away towards the red end; and at the same time general absorption begins at the ultra-violet end and extends up to 4900 A.U. as the pressure of the gas is increased. With the increase of pressure the bands become darker, and a few more are added against the red end. In fact, these need not be considered to be new additions, but those that were previously very faint and are now reinforced on increasing the pressure. As can be clearly seen from the spectrograms, the general absorption band extends more and more with the increase of the pressure until at great pressures it extends up to the green, where the banded spectrum begins. If we compare figs. 5, 7, & 9 (Pl. XI.), showing the ultra-violet principal absorption bands, it would seem that this band shifts towards the less refrangible side with increase of atomic weight.

In making a spectrogram, a number of exposures were taken on a single plate with the vapour at different pressures,

and another exposure with the source of light alone to serve as comparison spectrum.

As for the dependence of absorption on temperature of the vapour, it will be seen that the absorption of bromine gradually increases from 30 to about 600° C., at which it absorbs almost the whole of the ultra-violet up to 2000 A.U.; and after this again the absorption falls, and it becomes more and more transparent to ultra-violet radiations. The middle of the absorption band is not therefore situated at about 4170 A.U., as was thought by Dobbie and Fox. Further, the temperature of the maximum absorption according to our experiments is nearly 600° C. In the case of chlorine, the absorption increases slightly towards the red end with rise of temperature, but towards the short wave-length side there is no change at all, as it is clearly seen from the photographs, maximum temperature in our experiments being 800° C. nearly. In the case of iodine, absorption increases with temperature up to 300° nearly, and at 300° the ultra-violet up to 3250 A.U. is completely absorbed, and above this temperature the vapour again transmits the ultra-violet radiation.

Explanation of Plate XI.

- | | | |
|---------|--|-------------------------------|
| Fig. 1. | Absorption of Chlorine. | } In the visible region. |
| 2. | " " Bromine. | |
| 3. | " " Iodine. | |
| 4. | Emission spectrum of Bromine. | |
| 5. | Absorption of Chlorine at ordinary temperatures but for different pressures. | } In the ultra-violet region. |
| 6. | " " Chlorine at different temperatures. | |
| 7. | " " Bromine at ordinary temperature but for different pressures. | |
| 8. | " " Bromine at different temperatures. | |
| 9. | " " Iodine at ordinary temperatures but for different pressures. | |
| 10. | " " Iodine at different temperatures. | |

It will be seen from these that with the greatest quantity of chlorine, absorption at ordinary temperatures did not extend above 2750 A.U., and in the case of bromine beyond 3450 A.U., while in the case of iodine it did not extend beyond 4100 A.U. The fact that the emission and absorption spectra of these vapours are not complementary might be due to different complexities of molecular structure of the vapours in the two cases. Further, Beer's law does not seem to hold good in the case of these vapours.

We are now investigating the absorption of these vapours in the infra-red region, the results of which will be published on completion of the work.

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FIG. 1.

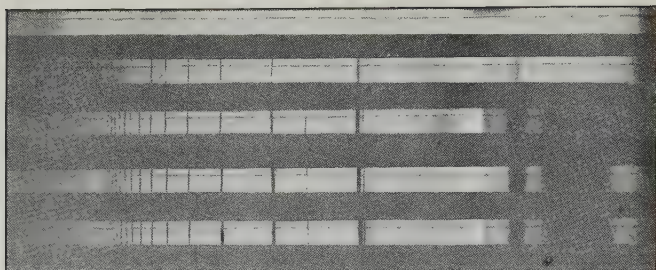
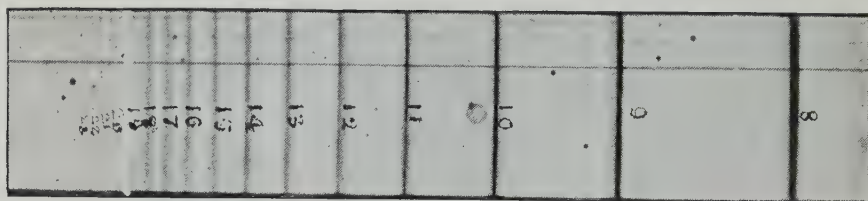


FIG. 2.

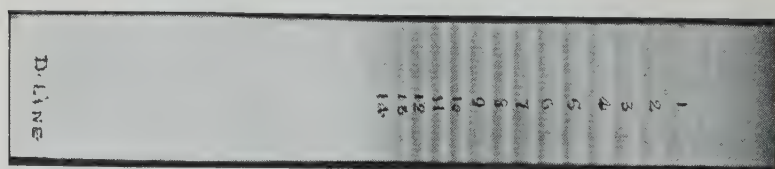


FIG. 3.



Enlarged photograph of a section of Fig. 2.

FIG. 5.



Channelled Spectrum.

FIG. 4.

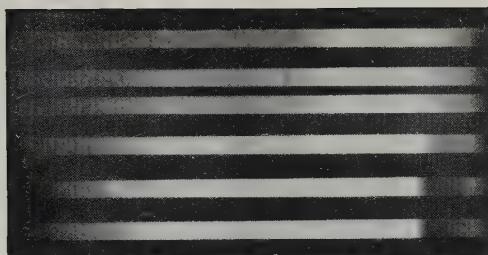
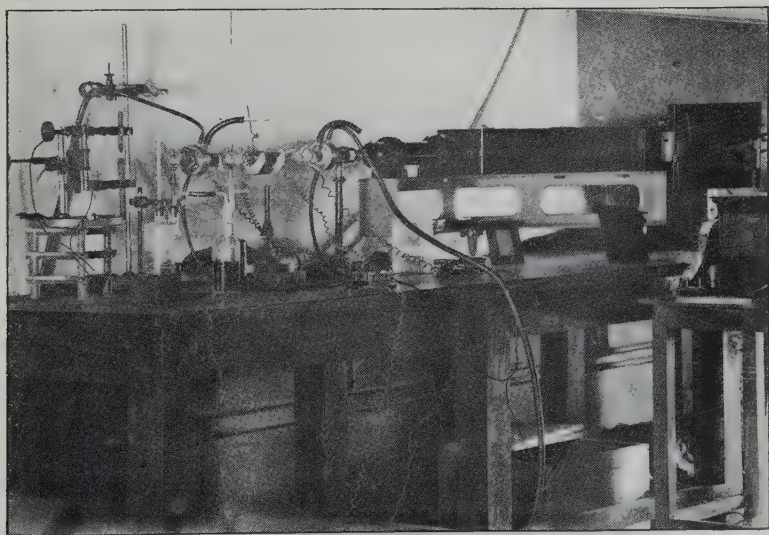


FIG. 6.



Apparatus as it stood in our study of the absorption of K-vapour.

LXXXIV. *Absorption of Potassium Vapour.* By
A. L. NARAYAN, M.A., A.Inst.P., and D. GUNNAYYA, B.A.*

[Plate XII.]

RECENT experiments of McLennan and Young on the absorption of light by the non-luminous vapours of Zinc, Cadmium, &c., have shown that our knowledge of the structure of molecules may be increased by a study of the optical properties of the vapours of the various elements at low temperatures; for, as Prof. McLennan remarked in the Guthrie Lecture on the Origin of Spectra, March 22, 1918, for the elements for which the principal series $\gamma = (1.5 S) - (mP)$, it is found that the wave-lengths of this series are strongly absorbed by their non-luminous vapours. And it is beyond doubt that there is a profound and intrinsic link between absorption and dispersion and the structure of the molecule of an element. A careful study of the optical and magneto-optical properties, especially absorption and dispersion of vapours of the elements, will be a most important step towards the exploration of the intimate structure of the molecule.

A very complete study of the optical and magneto-optical properties of sodium vapour was made by Prof. Wood, in which the periodicities of the vibrating mechanisms were studied in a variety of ways by absorption and by powerful stimulation of the vapour with white and monochromatic light. Investigation of the absorption spectrum of sodium vapour (Phil. Mag. 1908 & 1909) by Prof. Wood raised the number of members of the principal series from the seven previously known to 48, the largest number absorbed for any element thus far; and the late Dr. P. V. Bevan applied Wood's method to the other alkali metals, and observed extended Balmer series in Li, K, Rb, Ce (Proc. Phys. Soc. 1909; Proc. Roy. Soc. 1910 & 1911). It will be seen that the number of members of the principal series in potassium was raised to 26, considerably less than the number in the other alkali metals. In view of the similarity between the absorption spectra of the different alkali metals, it was thought very desirable first to extend to the non-luminous potassium vapour, studies along the same line. The following investigation was therefore undertaken to study the absorption of potassium vapour at different temperatures.

The apparatus consists, as shown in the photographic reproduction (Pl. XII. fig. 6), of a thin seamless steel tubing

* Communicated by the Authors.

about 30 inches long and about 1 inch in diameter. The tube was furnished with two water boxes against the ends, and two small lateral tubes were brazed into the steel wall, one at each end, for connexion with the Fluess pump and gas generator. The ends were closed with two quartz plates, cemented to the tube with best sealing-wax. The whole tube was mounted in a metal frame on a stand provided with levelling screws, so that the tube could be conveniently placed with its axis parallel to that of the collimator of the spectrograph. With the exception of a length of about 4 in. in the middle, the portion of the tube between the water boxes was covered with heating-coils kept red-hot during the experiment; and a continuous flow of cold water was maintained through the water boxes throughout the experiment.

A pretty large quantity of the fresh metal was cut into strips and introduced into the middle of the tube. Then, by connecting the tube to a gas generator, dry hydrogen gas was passed through the tube for some time, and thus the potassium was kept in a hydrogen atmosphere. With the metal in the centre of the tube and the heating-coils at the ends raised to redness, rapid distillation of the metal to the colder parts and the consequent deposition on the quartz windows could be prevented, and exposures of any length could be made under quite steady conditions.

In these experiments carbon arc was used as the source of light, since some of the lines in the arc spectrum serve as reference lines. The tube being mounted in position, light from the arc was concentrated by a quartz lens at the centre of the steel tube, and after emergence it was focussed by another quartz lens on the slit of the spectrograph. First, the current in the heating-coils was started, and 10 minutes after that the tube was heated at the centre by the flame of a Teclue burner, which gave a high temperature. When the tube was heated first, the absorption lines at the red end made their appearance, and as the temperature was raised the accompanying channelled spectrum developed. With the increase of temperature and the consequent increase of the density of the vapour the higher members of the Balmer series also developed. When the temperature and density of the vapour were sufficiently high to bring out the higher members of the series, it was found that the first two or three pairs of this series were immersed, so to speak, in a band spectrum, which was nothing but the accompanying channel spectrum subsequently developed into a dark band; and it was found by the authors that enormous increase in the

vapour-density was necessary to elicit the higher members of the series, the temperature of the tube being between 750° and 800° C. With the tube at this high temperature and with exposures of 1½ to 2 hours, the Balmer series could be extended to 30, and still higher temperatures were found to be of no avail; but when the temperature was raised still further to about 950° C., the highest we could command in the experiment, some slight traces of absorption in the first members of the diffuse series were suspected; and it is not possible to say anything definitely about the absorption of this series as, we are now continuing our experiments in that direction.

Balmer Series.

In the following table are given the wave-lengths of the principal series lines we observed from $m=11$ to $m=29$, together with the values of Dr. Bevan. In another column we have given the values calculated from the formulæ :

$$\text{O.F.} = 35005 \cdot 56 - \frac{109675}{\left\{ m + \cdot 293076 - \frac{\cdot 061356}{m-1} \right\}^2},$$

$$\text{O.F.} = 35005 \cdot 56 - \frac{109675}{\left\{ m + \cdot 296228 - \frac{\cdot 061628}{m-1} \right\}^2}.$$

Independent measurements of the lines beyond the 20th were made by three different observers separately by means of a comparator made by C. S. I. Co., and on subsequent comparisons the maximum difference between our observations amounted to .1 A.U.

No. m .	Authors.	Bevan.	Calculated.
11	2928·10	2928·00	2927·86
12	2916·45	2916·6	2916·38
13	2907·6	2907·6	2907·45
14	2900·00	2900·4	2900·38
15	2894·5	2894·6	2894·67
16	2889·85	2889·7	2890·00
17	2886·2	2885·9	2886·1
18	2883·00	2882·9	2882·8
19	2880·4	2880·3	2880·12
20	2878·00	2877·9	2877·8
21	2875·7	2875·8	2875·8
22	2874·15	2874·1	2873·99
23	2872·3	2872·5	2872·46
24	2871·2	2871·1	2871·12
25	2870·0	2870·0	2869·9
26	2869·1	...	2868·89
27	2868·15	...	2868·0
28	2867·4	...	2867·2
29	2866·7	...	2866·45

In the red channelled spectrum the wave-lengths of about 15 bands were measured by a Hilger wave-length spectrometer, and all the bands are clearly seen on the photographic reproduction and its enlargement. This spectrum was studied by Roscoe and Schuster (Proc. Roy. Soc. xxii. p. 362), and by Wood and Carter (Phys. Review, xxvii. p. 113, 1908). The wave-lengths of the bands as measured by us are given in the following table. (For photographing the spectra we used Schumann plates and Wratten & Wainwright Allochrome plates, specially sensitive to actinic radiations.)

The red channelled spectrum.

No.	Wave-length.	No.	Wave-length.
1	6811·0	9	6488·5
2	6760·0	10	6443·0
3	6711·0	11	6412·0
4	6661·0	12	6388·8
5	6622·0	13	6366·1
6	6584·0	14	6332·2 (not
7	6544·1		clearly seen in
8	6506·0		the photograph).

Explanation of Plate XII.

- Fig. 1. Principal series lines for gradually increasing densities.
 2. " " " " with greatest vapour-density; Temp. of tube = 100° C.
 3. Enlarged photograph of a portion of No. 2.
 4. Absorption in the visible region, showing the gradual development of the red channelled spectrum and its subsequent change to a dark band.
 5. Enlarged photograph of the same channelled spectrum, showing the 14 bands observed.
 6. Apparatus, etc.

In conclusion, we wish to express our best thanks to Mr. G. Subrahmanyam, B.A., of the Physics Department, for the very valuable assistance he has given during the progress of the work.

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LXXXV. *On the Aeration of Quiescent Columns of Distilled Water and of Solutions of Sodium Chloride.* By Professor W. E. ADENEY, *A.R.C.Sc.I., D.Sc., F.I.C.*, Dr. A. G. G. LEONARD, *F.R.C.Sc.I., B.Sc., F.I.C.*, and A. RICHARDSON, *A.R.C.Sc.I., A.I.C.**

Introductory.

IN the course of his investigations on the downward transmission of atmospheric gases through quiescent columns of water five feet in depth, one of the authors showed that, as the oxygen and nitrogen are dissolved at the exposed surface of the water, they do not remain concentrated in the surface layer, but are distributed through the lower layers with comparative rapidity.

From the fact that the distribution of the dissolved gases, at various depths, after a comparatively short time was almost uniform, it appeared impossible to account for it on the assumption that it was entirely due to such an extremely slow process as that of the diffusion of the dissolved gases from the saturated surface layer.

In addition to diffusion, it was suggested that a process of downward "streaming" of the exposed layer of water occurs; and that it results largely, though possibly not wholly, from an increase in its density, which, in the case of distilled water, is caused by the lowering of temperature attending evaporation, and, in the case of salt solutions, by this factor and that of concentration.

The downward streaming sets up a process of mixing of the constantly changing air-saturated surface layer with the lower layers of the water. When a slow stream of dry air is continuously passed over the exposed layer of a column of water, surface density changes are constantly occurring, and comparatively rapid mixing ensues, with the result that, if the water be de-aerated at the commencement of the experiment, it becomes re-aerated with comparative rapidity †.

The experiments described in this investigation have been carried out with the object of investigating the process of the aeration of de-aerated columns of water to a depth of ten feet. Columns of de-aerated distilled water and of solutions of sodium chloride were exposed to a slow stream

* Communicated by the Authors. Reprinted from the Proceedings of the Royal Dublin Society, vol. xvii. (n.s.).

† "Unrecognized Factors in the Transmission of Gases through Water." By W. E. Adeney, Trans. R. D. S. p. 161, 1905; and Phil. Mag. March 1905.

of dry air for periods of from two to eight weeks, when samples at different depths were drawn off, and the nitrogen content of each determined.

In general, it was found that re-aeration proceeded more rapidly in salt solutions than in pure water*, and a further series of experiments was carried out with solutions of sodium chloride, having a wide range of concentration, to ascertain the effect of concentration of the sodium chloride on the rate of aeration.

Experimental.

The de-aeration of the water employed in these experiments was effected by distillation *in vacuo*. In order to obtain water quite free from atmospheric gases, the distillation was at first carried on in a very slow current of hydrogen or of carbon dioxide; but, although the resulting water was air-free, it was always found to contain undesirable traces of hydrogen or of carbon dioxide, according to which gas was employed during the distillation. It was consequently decided to rely upon distillation under the reduced pressure obtained with the aid of a good water vacuum pump, employing a slow current of air, filtered through glass wool, to overcome difficulties from "bumping." The nitrogen content of the de-aerated water obtained did not exceed 1 c.c. per litre, which, in the case of pure water, amounts to about 7 per cent. of saturation at 15° C.

It was found unnecessary to determine the nitrogen content of each sample of water at the commencement of each aeration experiment, as it was found to be practically constant immediately after the de-aeration.

The glass tubes used in the experiments were about 3 cms. in diameter, and varied from 9 to 12 feet in length. T-pieces were fused on, at regular intervals, along the length of the tube, for drawing off samples of the water columns at different levels, and the lower ends of the tubes were sealed. The upper end of the tube was closed by a rubber stopper, fitted with an inlet and outlet tube, by means of which connexions were made to the pump and distilling apparatus; so that the water could be distilled directly into the experimental tube when desired.

In the case of salt solutions, the required quantity of sodium chloride was placed in a five-litre flask, connected with the vacuum distilling apparatus by means of a thick-wall rubber tube, and the required volume of pure water was allowed to distil into the flask and dissolve the salt, the

* See above references.

exact concentration of the solution being subsequently determined by analysis. A screw clip was then used to close the connexion with the pump, the flask detached with its rubber connecting tube, and attached, with the aid of the same connecting tube, to the experimental tube. When the free end of this connecting tube was completely filled with freshly distilled water, it could be attached air-free to the previously exhausted experimental tube. After attaching the flask to the tube, the latter could be filled by inverting the flask and unscrewing the clip, when the solution flowed into the tube.

Experimental tubes were also employed, which were furnished with quill capillary tubes, instead of side tubes, for drawing off samples. These tubes passed upwards through a rubber stopper at the bottom of the experimental tube to different levels inside, the external ends being attached each to a piece of thick-walled rubber tubing closed by a screw clip.

Each experimental tube was attached to a stout lath of wood for facility of removal from one laboratory to another. The room in which the aeration was carried out was one which received no direct sunshine nor heat from artificial sources, so that the temperature prevailing in it was not subject to sudden fluctuations. In the earlier experiments, a zinc cylinder, 14 inches in diameter and filled with water, was used as a jacket for the tubes. But it was subsequently found that a good wrapping of asbestos cloth was a sufficient guard against sudden variation in temperature. Manipulative difficulties were thereby considerably reduced, and it was possible to work with a greater number of tubes simultaneously.

A recording thermometer was kept in the room, and the greatest variation in temperature in the room, during the exposure of any one tube, did not exceed $4^{\circ}\cdot5$ C. This variation, however, was exceedingly slow—too slow to give rise to convection currents.

The air passing over the surface of the water in the tubes was first dried by calcium chloride; and the inlet tube was so arranged that the air did not play directly on to the surface. The inlet and outlet tubes were fixed at a distance of 1.5 to 2 inches above the water. The moist air issuing from the tube was passed through weighed CaCl_2 tubes, so that the amount of water evaporated could be determined for each tube. In most of the experiments three tubes were connected in series, drying-tubes being placed so that the moist air from one was dried before entering the succeeding tube.

A filter pump, worked by a constant head of water, seven

feet in height, was at first employed to aspirate the current of air through the tubes, but subsequently, owing to shortage of the town water supply, caused by the drought last summer, a different arrangement had to be substituted. An electrically driven small air pump was utilized to force air into a large glass vessel, which acted as an equalizer, and thence through the drying vessels and experimental tubes. This arrangement worked very satisfactorily.

The experimental tubes, having been filled with de-aerated water, were fixed in a vertical position; the stoppers, which had been used during filling, were removed, and were replaced by others carrying inlet and outlet tubes for the air current. The air current was continued for two or three weeks in the case of salt solutions, and three to eight weeks for pure water. The apparatus employed for the determination of the dissolved gases was of the form devised by one of the authors*.

*Method of withdrawing Samples from
the Experimental Tubes.*

Samples of water were withdrawn from an experimental tube, without at any time allowing them to come into contact with the air, with the aid of a modification of the gas burette used for the analysis of the dissolved gases.

By lowering the mercury reservoir, attached to the burette, a known volume of water was drawn from the tube into the latter, and thence transferred to a Plimpton gas holder to await examination. The depth from which the sample was drawn and the temperature of the water were at the same time noted. 50 c.c. of water were usually taken for the extraction and analysis of the dissolved gases in the case of the surface layer; and 100 c.c. for samples drawn from lower levels.

*Determination of Saturation Values for Nitrogen
of Sodium Chloride Solutions.*

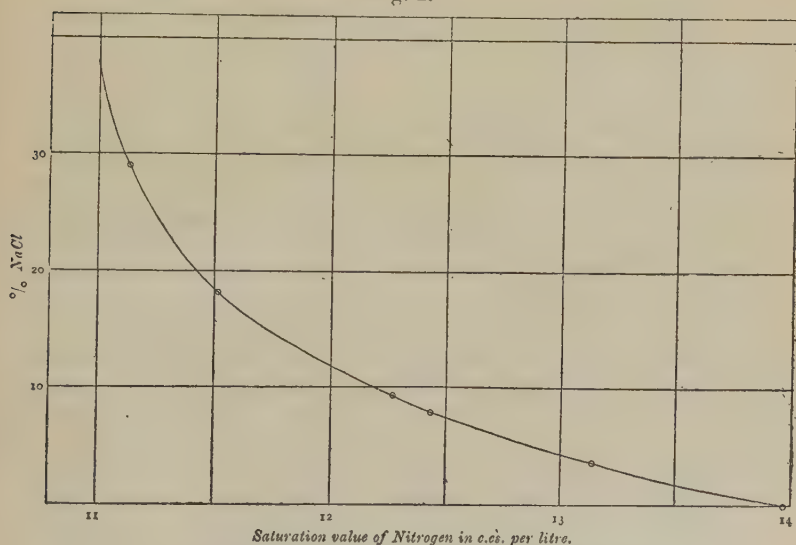
In order to calculate in percentages of saturation the observed rates of solution of atmospheric nitrogen by solutions of sodium chloride of the various concentrations employed in this investigation, it was necessary to determine the saturation values for atmospheric nitrogen of each solution. This was done by filling large tubes, about 5 cms. in diameter and 30 cms. in length, about two-thirds full of the salt solution. A current of air, previously passed through a glass

* Sci. Trans. R. D. S. vol. v. series 11, p. 548; also Supplemental vol. vi., Fifth Report of the Royal Commission on Sewage Disposal, p. 99.

wool filter and through distilled water to saturate it with aqueous vapour, was drawn through the solution under examination. The inlet tube reached to the bottom of the solution; and the apparatus was immersed in a thermostat. The current of air was continued for a sufficient time to ensure equilibrium being reached throughout the tube at the observed temperature. The dissolved nitrogen and the sodium chloride in the solution were then estimated.

The experimental results are shown by the accompanying curve (fig. 1).

Fig. 1.



Saturation values of Nitrogen in solutions of varying NaCl concentration at 15° C.

Method of expressing Experimental Results for the Purpose of Comparison.

The columns of water employed in these experiments were so deep—about ten feet—and the exposure of them to the air had to be continued over such extended periods of time—two to eight weeks—that it was decided not to attempt to control the temperature obtaining during the conduct of the experiments beyond preserving the room in which they were carried out, and which was exceptionally well circumstanced for such purpose, at as closely uniform temperature as possible during a set of experiments.

To have provided the means for controlling, at will, the temperature at which these experiments could be started and

continued would have added very considerably to the practical difficulties of an already sufficiently laborious problem; and it was not thought necessary to attempt to do so, since the authors had good reasons, which will be explained later on, for assuming that when the gas concentrations of a de-aerated column of distilled water, or of a solution of a salt, at any time during re-aeration were expressed in percentages of saturation, they would be found to increase practically in the same proportions at different temperatures, provided that the variation in temperature did not exceed 3° or 4° C.

This view was based upon the following considerations:—

(1) Dittmar has determined the saturation values of distilled and of sea-water for atmospheric nitrogen and oxygen between 4° C. and 35° C.; and when his results are plotted against temperatures, the curves obtained approximate to parallel straight lines between the limits 8° C. and 35° C.*.

(2) Adeney and Becker, in their work on the rate of solution of these atmospheric gases by distilled and by sea water, found that, when the experimental observations from zero to saturation were expressed as percentages of saturation and plotted against time, the curves obtained were coincident when uniform conditions of exposure of water to the gas, of the mixing of the exposed with the unexposed portions of the water, and of temperature (within 1° C.) obtained †.

It may be assumed from this that the curves showing the rate of solution of atmospheric nitrogen and oxygen by dilutions of sea-water with varying proportions of distilled water would also be coincident with the curves showing the same for distilled and sea-water, separately, under like conditions of exposure to air, of mixing, and of temperature varying within 1° C.

(3) Adeney and Becker further found that the curves showing the rate of solution in water of nitrogen and of oxygen, when stated in percentages of saturation, lie very closely together for differences of 5° C. within the range of temperature from 0° C. to 30° C.

Consequently it is possible to convert approximately, by simple calculation, observations made at slightly different temperatures, to those that would obtain at a selected common temperature, varying even to as much as 2 or 3 degrees from them, and still obtain sufficiently accurate results for purposes of comparison.

* Supplementary vol. vi. to the Fifth Report, Royal Commission on Sewage Disposal, p. 59.

† "The Determination of the Rate of Solution of Atmospheric Nitrogen and Oxygen by Water." By W. E. Adeney and H. G. Becker, Part 1, Sci. Proc. R. D. S. 1918, and Phil. Mag. April 1920, p. 385.

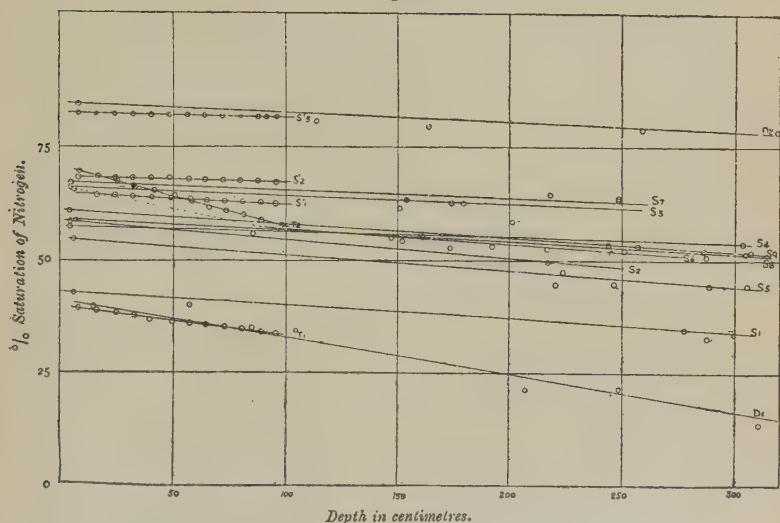
Experimental Results.

The conditions obtaining in some experiments with columns of salt solutions and of distilled water are given in the table on page 842.

Curves showing the nitrogen content of columns of distilled water, and of salt solutions, at different depths, expressed as percentages of saturation, are given in fig. 2.

On comparing the curves D_1 for distilled water (exposed to the air for twenty-seven days) and S_1 , for a 3.3 per cent.

Fig. 2.



Nitrogen content expressed in percentages of saturation at different depths below the surface.

salt solution (fourteen days), the effect of the salt on the progress of aeration is well illustrated. The curve for the distilled water column shows a fall in nitrogen content from 40 per cent. at the surface to 13 per cent. at a depth of 311 cms., whereas the corresponding values for the 3.3 per cent. salt solution ranged from 42.7 to 38.3 per cent. respectively in about half the time.

Even with a solution containing only 0.0116 per cent. sodium chloride (curve S_9), the effect of the salt in solution is well marked.

The curves S_1' , S_2' , S_3' , T_1 , and T_2 are plotted from results

	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	S ₈	S ₉	D ₁	D ₂
Initial concn. of N. in c.c. per litre	0.9	0.662	0.662	0.662	0.618	0.618	0.618	0.618	0.618	1.06	0.618
Initial concn. of N. as percentage of saturation }	8.85	6.22	5.17	5.08	4.74	4.66	4.36	4.76	4.74	6.92	4.65
Percentage of NaCl	3.303	1.97	0.94	0.41	0.25	0.116	0.063	0.029	0.0116	0	0
Temp. of room when set up	11.8° C.	11.8° C.	13° C.	—	13.4° C.	14.0° C.	17.2° C.	17.8° C.	17.4° C.	9.5° C.	14.1° C.
Temp. when taking samples	10° C.	11.2° C.	12.7° C.	15.2° C.	16.7° C.	16.9° C.	20.4° C.	20° C.	18.8° C.	10.2° C.	17.9° C.
Time in days.....	14	17	18	18	18	18	19	21	23	27	56
Water evap. in gms.	—	—	12.07	10.815	6.212	7.632	6.915	7.98	8.3536	—	25.18
Saturation value of N. from curve at 15° C. in c.c. per litre	11.17	11.44	12.27	13.09	13.41	13.72	13.81	13.91	13.94	—	—
Saturation value of N. at temperature of experi- ment in c.c. per litre...	12.27	12.28	12.79	13.037	13.02	13.26	12.59	12.97	13.047	15.31	13.29
Length of column in cms.	317	269	269	317	317	269	269	317	347	360	347
Litres of air drawn over ...	—	—	1024	843	452	542	398	456	481	—	1734
Litres of air per 24 hrs. ...	—	—	57	47	25	30	21	22	21	—	31

obtained from observations with columns of sea and tap water, 3 feet deep and 4 cms. diameter. The columns were exposed to the air at temperatures 14° , 12° , 13.5° , 13° , and 13.5° C. for 7, 6.75, 11, 4, and 7 days respectively.

Samples of the salt solutions from the top and bottom layers of the columns, after aeration, were carefully examined by means of a Pulfrich refractometer to ascertain whether any difference in concentration of the sodium chloride existed between the two layers, but no difference could be detected.

In order to compare more clearly the experimental results obtained for the salt solution, an approximate correction for slight variations in the length of time of their exposure to the air has been made. Eighteen days was taken as the standard time, since four out of the nine tubes were exposed for that time.

Adeney and Becker's formula for calculating the rate of re-aeration was employed, viz. :—

$$w = (100 - w_1) \left(1 - e^{-f \cdot \frac{a}{v} t} \right),$$

where w = amount of gas dissolved, expressed in percentage of saturation.

w_1 = initial concentration in percentage of saturation.

f = coefficient of escape of the gas from the liquid per unit area and volume.

v = volume of liquid.

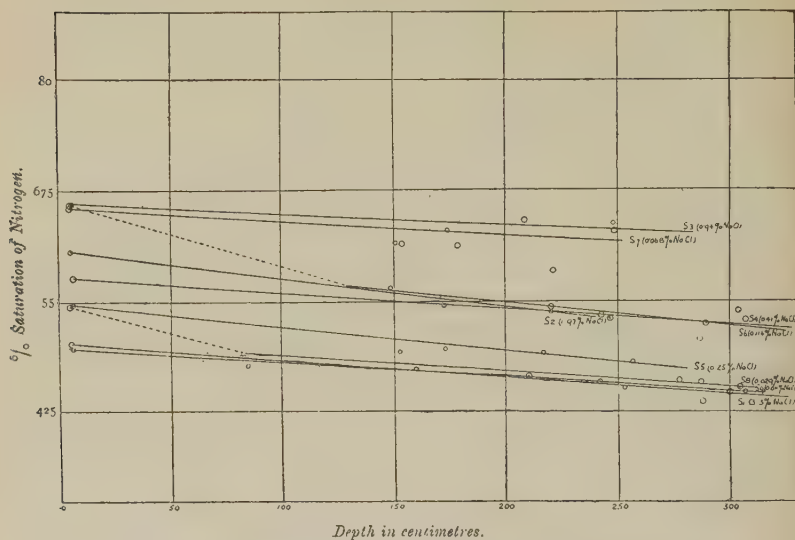
a = area of surface.

t = time of exposure.

By means of the above equation, if w be known for any time t , its value can be found for any other time t . The mean value of the concentration of the gases in solution in the liquid was taken to be w . The actual values at various depths were afterwards calculated. Curves were plotted for the columns of solutions, using observations made after eighteen days. They are given in fig. 3.

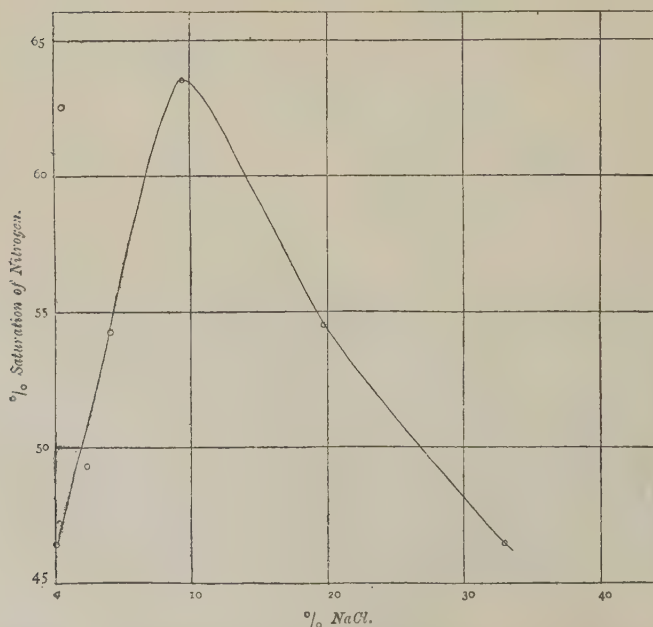
The values for the concentrations of nitrogen at a depth of 200 cms. were taken, and these values were plotted against the concentration of salt. The maximum concentration of

Fig. 3.



Concentration of Nitrogen at various depths after 18 days' exposure for different salt solutions.

Fig. 4.



Relation between NaCl concentration and downward "streaming" of dissolved Nitrogen to depths of 200 cms. through solutions of that salt.

nitrogen was found to obtain in a solution with a concentration of about 1 per cent. of sodium chloride. The curves obtained are given in fig. 4.

Conclusions.

The following conclusions may be drawn from the experimental results obtained in this investigation :—

1. The aeration of quiescent bodies of water, fresh and salt, under natural conditions is effected by a process of mixing of the exposed layer with the unexposed portions of the water to depths of at least 10 feet.

2. The process of mixing is caused by the downward "streaming" by the constantly changing layer of water exposed to the air. This downward "streaming" sets up a process of mixing certainly to depths of 10 feet, and in all probability to much greater depths.

3. The process of mixing set up by the downward "streaming" proceeds more rapidly, and more uniformly downwards, to depths of at least 10 feet, in salt water than in fresh water.

4. The rate at which the "streaming" proceeds depends largely, though not wholly, upon the rate at which the concentration and cooling of the surface layer of the water is brought about by evaporation from it.

5. The process of "streaming," and consequently of mixing, also proceeds more rapidly at temperatures at and above 10°C . than below it. It is distinctly less rapid and less uniform downwards to 10 feet deep, and probably to greater depths, at temperatures below 8°C ., especially in fresh waters.

6. The rate at which the process of mixing from "streaming" proceeds also depends upon the concentration of salt in solution. The optimum concentration appears to be about 1 per cent. sodium chloride.

This last conclusion is based upon one series of experiments only, and should be confirmed by further experiments which the authors hope shortly to carry out.

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LXXXVI. *Tables of the Bessel Function $I_n(x)$.* By HUGH E. H. WRINCH, *M.I.Mech.E.*, and DOROTHY WRINCH, *D.Sc.*, *Fellow of Girton College, Cambridge, and Member of the Research Staff, University College, London* *.

WHILE Tables of the Bessel Functions of both kinds, $J_n(x)$ and $Y_n(x)$, are now fairly complete, much work remains to be done in regard to the corresponding tables for the so-called "Functions of Imaginary Argument," $I_n(x)$ and $K_n(x)$, which are of considerable importance in physics.

In the present paper we give a table of the values of $I_n(x)$, where $n=0, 1, \dots, 6$, at intervals of a unit, and $x=5, 6, 7, \dots, 15$, at intervals of a unit.

The function may be defined by

$$I_\eta(x) = \iota^{-\eta} J_\eta(i x), \quad (\iota = \sqrt{-1}),$$

$$= \frac{x^\eta}{2^\eta \Gamma(\eta+1)} \left\{ 1 + \frac{x^2}{2^2 1! \eta+1} + \frac{x^4}{2^4 2! \eta+1 \eta+2} + \dots \right\},$$

and for large values of x , it possesses the asymptotic expansion,

$$I_\eta(x) = \frac{e^x}{\sqrt{2\pi x}} \left\{ 1 + \frac{1^2 - 4\eta^2}{1! 8x} + \frac{(1^2 - 4\eta^2)(3^2 - 4\eta^2)}{2! (8x)^2} + \dots \right\}.$$

Previous tables of this function have been almost entirely limited to the functions $I_0(x)$, $I_1(x)$ of orders unity and zero. The British Association report for 1896 gives $I_0(x)$ to nine places from $x=0$ to 5.100 at intervals of 0.001, following on a table of $I_0(x)$ of the same character in 1893. Aldis (1899) † gives $I_0(x)$ and $I_1(x)$ to twenty-one places at intervals of 0.1 from $x=0$ to $x=6$, and a few extra values.

Alding (Leipzig, 1911) published tables of the logarithms of these functions, $I_0(x)$, $I_1(x)$, from $x=0$ to 10, at intervals of 0.01. The British Association Committee in 1889 published some tables of the more general function $I_n(x)$ to twelve figures for $n=0, 1, 2, \dots, 11$, $x=0$ to 6, with intervals 0.2 in x . These were calculated from $I_0(x)$ and $I_1(x)$ by the use of the recurrence formula,

$$I_{\eta-1}(x) - I_{\eta+1}(x) = \frac{2\eta}{x} I_\eta(x).$$

For a complete bibliography of the subject, reference may be made to Watson's 'Theory of Bessel Functions,' p. 655.

* Communicated by the Authors.

† Proc. Roy. Soc. lxiv. p. 218 (1899).

Tables of the Bessel Function $I_n(x)$.TABLE I.— $I_n(x)$.

x .	$I_0(x)$.	$I_1(x)$.	$I_2(x)$.	$I_3(x)$.	$I_4(x)$.	$I_5(x)$.	$I_6(x)$.
5.0	27.2400	24.3353	17.5062	10.3307	5.1087	2.15643	.797805
6.0	67.2337	61.3426	46.7862	30.1509	16.6373	7.96810	3.35623
7.0	168.591	156.039	124.009	85.1770	51.0027	26.8854	12.5952
8.0	427.562	399.875	327.599	236.078	150.536	85.5419	43.61815
9.0	1093.59	1030.92	864.500	646.694	433.360	261.479	142.830
10.0	2815.69	2671.02	2281.52	1758.39	1226.47	777.171	449.274
11.0	7288.49	6948.85	6025.05	4757.93	3429.81	2263.59	1372.05
12.0	18949.0	18141.4	15925.5	12832.8	9508.82	6493.73	4097.54
13.0	49444.5	47502.6	42136.0	34538.3	26195.5	18417.5	12028.4
14.0	129419	124707	111603	92821.3	71823.3	51778.1	34887.1
15.0	339646	328126	295901	249217	196212	144568	99826.9

A demerit of the recurrence formula is the accumulation of the errors, which ultimately, as in all such cases, renders it unsatisfactory in that the possible error cannot be specified.

The tables we now give were calculated directly from the asymptotic expansion, and the recurrence formula was only used as a check at suitable intervals. When used in this way, it leaves nothing to be desired.

The resulting tables are in all cases correct to five significant figures. Six figures are given, and are usually correct, though the sixth figure must be regarded as approximate.

TABLE II.—Log $\Gamma(x+1)$.

x .	Log $\Gamma(x+1)$.	x .	Log $\Gamma(x+1)$.
1	·0000000	15	12·1164997
2	·3010300	16	13·3206197
3	·7781513	17	14·5510686
4	1·3802113	18	15·8063411
5	2·0791813	19	17·0850947
6	2·8573326	20	18·3861247
7	3·7024306	21	19·7083440
8	4·6055206	22	21·0507667
9	5·5597631	23	22·4124945
10	6·5597631	24	23·7927057
11	7·6011558	25	25·1906457
12	8·6803370	26	26·6056190
13	9·7942804	27	28·0369828
14	10·9404084	28	29·4841408

TABLE III.

x .	$\sqrt{2\pi x}$.	e^x .	e^{-x} .	$\frac{e^x}{\sqrt{2\pi x}}$.	$\frac{e^{-x}}{\sqrt{2\pi x}}$.
1	2·50663	2·71828	·367879	1·08444	·146763
2	3·54491	7·38905	·135335	2·08441	·038177
3	4·34161	20·0855	·049787	4·62629	·011467
4	5·01326	54·5981	·018316	10·8908	·003653
5	5·60499	148·413	·006738	26·4787	·001202
6	6·13996	403·429	·002479	65·7055	·000404
7	6·63191	1096·63	·000912	165·357	·000137
8	7·08981	2980·96	·000335	420·456	·000047
9	7·51989	8103·08	·000123	1077·55	·000016
10	7·92665	22026·5	·000045	2778·78	·000006
11	8·31355	59874·1	·000017	7202·00	·000002
12	8·68321	162755	·000006	18743·6	·000001
13	9·03778	442414	·000002	48951·6	·000000
14	9·37894	120260	·000001	128224	
15	9·70813	326902	·000000	336730	
16	10·0265	888611	886261	
17	10·3351	241549	233718	
18	10·6347	656600	617411	
19	10·9261	178482	163354	
20	11·2100	485165	432797	

Certain subsidiary tables are also given, whose calculation was a necessary preliminary. They are of types which are frequently needed. Table II., for example, gives the values of $\log \Gamma(n+1)$ or $\log (n!)$ from $n=1$ to 28, to seven significant figures. They are calculated from the seven figure logarithms of Chambers, and therefore should certainly be correct to five significant figures.

Table III. is of the same type as a table given in Jahnke and Emde's 'Funktionentafeln' (Leipzig and Berlin, 1909). It gives the values of e^x , e^{-x} , $e^x/\sqrt{2\pi x}$, $e^{-x}/\sqrt{2\pi x}$ from $x=1, 2, 3, \dots 20$.

LXXXVII. *The Calculation of the Electric Moment of the Molecule of a Substance.* By CHARLES P. SMYTH, Ph.D., Department of Chemistry, Princeton University*.

THE system of electrons and positive nuclei constituting a molecule may be regarded as an electric doublet. This doublet may be very small, or it may be so large that its charges tend toward separation by ionization. According to the magnitude of this doublet as exhibited in the properties of a substance, the substance is qualitatively classified as polar or non-polar †. Inasmuch as the doublet in a molecule may be neither very small nor very large, the classification is not a sharp one. The actual measure of the magnitude of a doublet is its electric moment, a quantity which has been determined for the molecules of very few substances. The electric moment of a molecule may be defined as the product of the distance between the "centres of gravity" of the positive and negative constituents of the molecule by the total charge of either sign. A knowledge of its value is of obvious interest in testing theories of molecular structure and also in leading to a precise explanation of those properties of a substance which lead to its classification as polar or non-polar.

The present paper, which has been developed in connexion with an experimental investigation of the subject, describes a method by which the moments of the permanent electric doublets in the molecules of many substances may be calculated from data already available.

* Communicated by Prof. K. T. Compton.

† G. N. Lewis, Jour. Amer. Chem. Soc. xxxviii. p. 762 (1916); xxxv. p. 1448 (1913). W. C. Bray and G. E. K. Branch, Jour. Amer. Chem. Soc. xxxv. p. 1440 (1913).

EQUATIONS OF DEBYE AND THOMSON.

It has been found that the existence of a permanent electric doublet in the molecule of a substance contributes to the value of the dielectric constant of the substance, when the molecule is free to move, owing to the tendency of the molecule to orient itself in the electric field, thus adding to the electric polarization of the medium. When the molecule is rigidly constrained and unable thus to orient itself, as in solids, this contribution disappears. The relation was first formulated by Debye* for gases at constant volume:

$$\epsilon = \epsilon_0 + \frac{a}{T}, \quad (1)$$

in which ϵ is the dielectric constant, T the absolute temperature, and ϵ_0 and a are constants, the term $\frac{a}{T}$ containing the contribution of the moments of the permanent doublets. For liquids, the expression developed was

$$\frac{\epsilon - 1}{\epsilon + 2} = b + \frac{a}{T} (2)$$

b and a are assumed to be constant for a given liquid, a being connected with the electric moment μ by the expression

$$\mu = \frac{3}{\sqrt{4\pi}} \sqrt{\frac{ka}{N}}, \text{ in which } k \text{ is the Boltzmann-Planck}$$

constant and N the number of molecules per cm^3 . In the development of this equation, the change in volume accompanying change in temperature of the liquid is treated as negligible, and it is assumed that the molecule has a permanent electric moment upon which an induced moment may be superimposed by the application of an external electric field. The equation takes account of the orienting influence of the molecules upon one another because of their electric fields only by including the average field due to doublets at a considerable distance from the region under consideration.

Thomson† has derived an equation for gases similar to that given by Debye. It is assumed that the density of the gas is constant and equal to the density when the temperature is 0°C . and the pressure 760 mm. The equation then is

$$\epsilon = a + \frac{.88\mu^2 \times 10^{36}}{T}, \quad (1a)$$

where ϵ , μ , and T have their usual significance, and a is a

* P. Debye, *Phys. Zeit.* xiii. p. 97 (1912).

† J. J. Thomson, *Phil. Mag.* (6th series), xxvii. p. 757 (1914).

constant assumed to be independent of temperature. The numerical factor comes as the result of replacing all universal constants by their numerical values. If ϵ_1 and ϵ_2 are the values of the dielectric constant at the temperatures T_1 and T_2 , substitution in the above equation and subtraction gives the equation

$$\epsilon_1 - \epsilon_2 = .88\mu^2 \times 10^{36} \left(\frac{1}{T_1} - \frac{1}{T_2} \right), \quad \dots \quad (3)$$

from which μ may be calculated directly.

EQUATION OF GANS.

A more general equation has been developed by Gans* and discussed and tested by Gans and Isnardi†. This equation is developed on the assumption that the molecule has a permanent electric moment upon which an induced moment may be superimposed, and it takes account of the mutual influence of the molecules on the assumption that the forces acting between them are isotropic. The equation may be written :

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{1}{D} = \frac{4\pi N_0}{3M} g + \frac{16\sqrt{\pi}\mu^2 N_0^2}{9RMT} \Phi(\tau), \quad \dots \quad (4)$$

in which D is the density ; N_0 is the number of molecules in one gram-molecule ; M is the molecular weight ; g is the constant of "quasi-elastic linking," that is, the moment induced in the molecule by unit exciting force ; R is the universal gas constant ; and

$$\begin{aligned} \tau = \frac{kT}{\mu E_0} &= \frac{3R}{4N_0^2\mu^2} \sqrt{\frac{s^3 M N_0}{\pi}} \cdot \frac{T\sqrt{1-\gamma D}}{\sqrt{D}} \\ &= \frac{T\sqrt{1-\gamma D}}{B\sqrt{D}}, \quad \dots \quad (5) \end{aligned}$$

where $\gamma = \frac{8\pi N_0 g^2}{3s^3 M}, \quad \dots \quad (6)$

$$B = \frac{3R}{4N_0^2\mu^2} \sqrt{\frac{s^3 M N_0}{\pi}}, \quad \dots \quad (7)$$

s = the smallest distance between the centres of two molecules,

* R. Gans, *Ann. d. Phys.* (4) lxiv. p. 481 (1921).

† H. Isnardi and R. Gans, *Phys. Zeits.* xxii. p. 230 (1921). H. Isnardi, *Zeits. f. Phys.* ix. p. 152 (1922); see also P. Lertes, *Zeits. f. Phys.* vi. p. 257 (1921).

that is, the molecular diameter; $k = \frac{R}{N_0}$, the Boltzmann-Planck constant, and $E_0 =$ the most probable molecular field. If we substitute

$$\frac{16 \sqrt{\pi} \mu^2 N_0^2}{9RM} = A \quad \dots \quad (8)$$

and

$$\frac{4\pi N_0}{3M} g = C, \quad \dots \quad (9)$$

the equation becomes

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{1}{D} = C + \frac{A}{T} \Phi \left(\frac{T \sqrt{1 - \gamma D}}{B \sqrt{D}} \right), \quad \dots \quad (10)$$

also

$$\gamma = \frac{8}{3\pi} \left(\frac{BC}{A} \right)^2 \quad \dots \quad (11)$$

C may be calculated from the dispersion curve for the visible region of the spectrum by means of the following equation:

$$\frac{m^2 - 1}{m^2 + 2} \frac{1}{D} = \frac{C}{1 - \frac{\lambda_0^2}{\lambda^2}}, \quad \dots \quad (12)$$

in which m is the index of refraction for light of wave-length λ , and λ_0 is the wave-length corresponding to a characteristic vibration frequency in the ultra-violet region.

$\Phi(\tau)$ is a function originally introduced by Gans* in his theory of paramagnetism as $\Phi(\tau) = \tau \psi(\tau)$. For small values of τ , $\psi(\tau)$ may be represented by the series

$$\psi = 1 - \frac{\tau \sqrt{\pi}}{2} + \frac{1}{60} (\pi \tau)^4 - \frac{1}{126} (\pi \tau)^6 + \frac{1}{240} (\pi \tau)^8 - \dots, \quad (13)$$

while for large values of τ ,

$$\psi = \frac{\sqrt{\pi}}{4\tau} \left(1 - \frac{1}{6\tau^2} + \frac{1}{18\tau^4} - \frac{1}{40\tau^6} + \dots \right), \quad \dots \quad (14)$$

For very large values of τ , that is, for high temperatures and low densities, as in the case of uncompressed gases, $\tau \psi(\tau)$ assumes the constant value $\frac{\sqrt{\pi}}{4}$, so that, for this special case,

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{1}{D} = C + \frac{A}{T} \frac{\sqrt{\pi}}{4}, \quad \dots \quad (10a)$$

* R. Gans, *Ann. d. Phys.* (4) 1. p. 163 (1916).

which is similar in form to equation (2), except for the presence of the factor $\frac{1}{D}$ on the left, which Debye, as an approximation, treated as constant for liquids.

In the original equation (10) the constants A and B, since γ can be expressed in terms of A, B, and C, are the only quantities which cannot be experimentally determined or calculated directly. By obtaining C from optical data, determining ϵ and D at several different temperatures, and successively substituting these values in the equation, A and B may be calculated by the method of successive approximations. μ is then obtained by means of equation (8).

Isnardi* has tested the validity of the equation for ether and chloroform over a wide range of temperature, and has further tested it on a number of other substances by calculating the dielectric constant in the vapour state from data for the liquid, obtaining good agreement between the calculated and the observed values. Lertes† has applied it successfully to chloroform and toluene.

The accuracy with which the equation represents the behaviour of these liquids is strong evidence of its validity. It is thus apparent that knowledge of the refractive indices of a substance for light of different wave-lengths (two or more) and of the densities and dielectric constants at a number of different temperatures makes possible the calculation of the electric moment of the molecule of the substance.

NEW METHOD OF CALCULATION.

In the present work, a somewhat different method has been developed for the calculation of the moment. In equation (4), $\tau\psi(\tau)$ may be substituted for $\Phi(\tau)$, and τ replaced by the expression given for it in (5). We then get

$$\frac{\epsilon-1}{\epsilon+2} \frac{1}{D} = \frac{4\pi N_0}{3M} g + \frac{4}{3} \sqrt{\frac{s^3 N_0}{M}} \sqrt{\frac{1-\gamma D}{D}} \psi(\tau).$$

Substitution for γ of its value obtained from equation (6) gives

$$\frac{\epsilon-1}{\epsilon+2} \frac{1}{D} = \frac{4\pi N_0}{3M} g + \frac{4}{3} \sqrt{\frac{s^3 N_0}{MD} - \frac{8\pi N_0^2 g^2}{3M^2}} \psi(\tau).$$

Substitution for g of its value obtained from equation (9) gives

$$\frac{\epsilon-1}{\epsilon+2} \frac{1}{D} = C + \frac{4}{3} \sqrt{\frac{s^3 N_0}{MD} - \frac{3C^2}{2\pi}} \psi(\tau). \quad . \quad . \quad (15)$$

* *Loc. cit.*

† *Loc. cit.*

For a given substance, ϵ , D , and $\psi(\tau)$ are the only variables contained in equation (15). The experimental determination of ϵ and D , accordingly, makes possible the calculation of the corresponding value of $\psi(\tau)$. From $\psi(\tau)$, the value of τ may be obtained by equations (13) and (14), and, with τ known, μ may be calculated.

In order to find τ from $\psi(\tau)$ we may use the solutions of equations (13) and (14), given by Gans*, as shown in Table I.

TABLE I.
Relation between τ and $\psi(\tau)$.

τ .	$\psi(\tau)$.	τ .	$\psi(\tau)$.
0.0	1.0000	3.0	0.1451
0.1	0.9115	3.3333	0.1310
0.2	0.8249	4.0	0.1097
0.25	0.7825	5.0	0.08806
0.5	0.6013	8.0	0.05526
1.0	0.3867	10	0.04425
1.25	0.3231	15	0.02953
1.4286	0.2883	20	0.02215
1.6667	0.2516	25	0.01773
2.0	0.2131	30	0.01477
2.5	0.1727	∞	0.00000

By plotting graphically on a large scale the values of $\psi(\tau)$ against those of τ , a curve is obtained from which the value of τ corresponding to any value of $\psi(\tau)$ may be accurately read off. Equation (15) thus provides a means of calculating τ .

To find the value of μ we substitute the value of γ from equation (6) into the third member of equation (5), giving

$$\tau = \frac{3RT}{4\mu^2 N_0^2} \sqrt{\frac{s^3 M}{\pi N_0 D} - \frac{8}{3} g^2}.$$

We next substitute the value of g from equation (9) and solve for μ , obtaining

$$\mu = \sqrt{\frac{3RT}{4N_0\tau}} \sqrt{\frac{s^3 M}{\pi N_0 D} - \frac{3M^2 C^2}{2\pi^2 N_0^2}}. \quad (16)$$

μ may thus be calculated from the value of τ corresponding to that of $\psi(\tau)$ obtained from equation (15). Equations (12), (15), and (16) render possible the calculation of μ , the

* R. Gans, *Ann. d. Phys.* lxiv. p. 498 (1921).

electric moment of the molecule of a substance, in the liquid or gaseous state, from the indices of refraction at two different wave-lengths, the density of the substance under the conditions under which these indices are measured, one value of the dielectric constant together with the temperature at which it is measured, the density at this temperature, the molecular diameter, the molecular weight, and certain universal constants. In order to calculate the moment through the constant A , as obtained by Isnardi and Gans (*cf.* equations (8) and (10)), it is necessary to have all of these data with the exception of the molecular diameter and the addition of the values of the dielectric constant and the corresponding density at a number of different temperatures. The necessary values of the refractive indices and the accompanying densities are available for a large proportion of the substances which may come up for consideration, but the dielectric constants of most substances have been measured within so small a temperature range as to make the method of Isnardi and Gans impracticable until our experimental knowledge of the temperature dependence of dielectric constants is considerably extended.

The molecular diameter, which is the only quantity required in this new method of calculation that is not required in the method used by Isnardi and Gans, has been defined as the smallest distance by which the centres of any two molecules can be separated. This is the molecular diameter as ordinarily used in the kinetic theory of gases, and may, therefore, be calculated from viscosity data or from the value of the constant b in van der Waals' equation. The values thus obtained are not always reliable *, and may, in some cases, introduce errors into the values of the moments calculated from them. Fortunately, however, a large error in the value of the diameter produces, as a rule, a relatively small error in the calculated value of the moment because of the form of the equations used.

Equations (15) and (16) contain two terms under the square root sign, the second of which, $\frac{3C^2}{2\pi}$ and $\frac{3M^2C^2}{2\pi^2N_0^2}$, are constant for any given substance and small in comparison with the first. In both equations, the first term under the square root sign is larger, the lower the density. For gases, therefore, the second term is quite negligible in comparison with the first and, indeed, for liquids, the error introduced by the omission of the second term from both equations is small.

* J. H. Jeans, 'Dynamical Theory of Gases,' chapter xiv.

RESULTS OBTAINED FROM THE DIFFERENT EQUATIONS.

The application of the different equations to various substances is illustrated by the results given in the following tables, in which the first column gives the temperature on the centigrade scale at which the value of the dielectric constant given in the second column is observed, while the third column gives the corresponding density, and the fourth column the calculated value of the moment multiplied by 10^{18} . The fifth column shows the method of calculation used, and includes any necessary explanation. The method described as "Eq. (15) and (16) simplified" is that in which the terms $\frac{3C^2}{2\pi}$ and $\frac{3M^2C^2}{2\pi^2N_0^2}$ are neglected. The similarity of equation (10a) to equation (2) has already been noted. When equation (10a) is used in the calculation of μ , the values of ϵ and D corresponding to the upper and lower limits of the temperature interval shown in the tables are substituted in the equation, C is eliminated between the two resulting simultaneous equations, and the constant A is thus obtained. μ is then calculated from A by means of equation (8). The calculation is similar to that involved in the use of equation (3), which Thomson proposes for gases, except that a variable density is introduced.

The values used for the universal constants are $N_0 = 6.07 \times 10^{23}$ and $R = 8.315 \times 10^7$. The molecular weight is reckoned for each substance from the atomic weights of its constituent elements. The values of C and s obtained for a substance are shown in the tables above the other data for that substance. When a different value of s is used in order to determine the effect of variation in s upon the value of μ , it is given in the fifth column.

Table II. shows that, except in the neighbourhood of the freezing-point of the liquid, equations (15) and (16) give a value for μ in excellent agreement with that obtained by Isnardi and Gans, $\mu = 1.435 \times 10^{-18}$. The use of the value 4.5×10^{-8} instead of 3.39×10^{-8} for the diameter makes an appreciable difference in the value of μ , but this difference is only slightly greater than that between the value 1.26×10^{-18} obtained by Isnardi for the moment of the chloroform molecule and the value 1.358×10^{-18} obtained by Lertes for the same quantity, chloroform being the only substance for which the moment has been obtained by the method of Isnardi and Gans by two different observers. The omission

TABLE II.

Ethyl Ether ($C=2.961$; $s=3.39 \times 10^{-8}$ cm.).

Temp. °C.	ϵ .	D.	$\mu \times 10^{18}$.	Method.
18	4.36	0.7150	1.308	Eq. (15) and (16) ($s=4.5 \times 10^{-8}$ cm.).
"	"	"	1.446	Eq. (15) and (16)
"	"	"	1.420	Eq. (15) and (16) simplified.
-120	3.16	0.8612	0.603	Eq. (15) and (16) simplified.
-100	8.143	0.8410	1.373	" " " " "
-80	7.049	0.8205	1.373	" " " " "
-54	6.33	0.7980	1.409	" " " " "
0	4.683	0.7359	1.410	" " " " "
18	4.36	0.7150	1.420	" " " " "
160	2.41	0.4927	1.420	" " " " "
100	1.00516	0.00242	1.513	Gas. Eq. (15) and (16) simplified.
Temp. Interval (°C.).				
-54 to 0		0.932	Eq. (10 a).	
0 to 18		0.383	" "	
40 to 100		1.000	" "	
140 to 160		1.133	" "	

The data on the liquid are taken from the paper of Isnardi and Gans (*Phys. Zeits.* xxii. p. 230 (1921)), and differ only slightly from those in the later paper of Isnardi (*Zeits. f. Phys.* ix. p. 152 (1922)). The value of ϵ for the gas is that given by K. Bädcker (*Zeits. Phys. Chem.* xxxvi. p. 304 (1901)), and the density is obtained approximately on the assumption that the vapour behaves as an ideal gas. The value $s=3.39 \times 10^{-8}$ cm. is that calculated by Isnardi and Gans, and is used here for the sake of comparison. The value $s=4.5 \times 10^{-8}$ cm. is obtained by application of the kinetic theory of gases to data contained in Landolt-Börnstein, 4th edition.

of the terms $\frac{3C^2}{2\pi}$ and $\frac{3M^2C^2}{2\pi^2N_0^2}$ has only a very small effect upon the value of μ , which justifies the use here of equations (15) and (16) in the simplified form. The results obtained by means of equation (10 a) are extremely variable, and differ widely from those given by the other methods. The values of μ calculated for ether at widely different temperatures show close agreement with the exception of the value at -120° , which is just below the generally accepted value for the freezing-point of the liquid. The value for the gas at 100° is calculated from an old value of ϵ and a calculated

value of D , and shows agreement which is surprisingly good under the circumstances.

TABLE III.

Hydrogen Sulphide ($C=0.220$).

Temp. °C.	ϵ .	D .	$\mu \times 10^{18}$.	Method.
10	5.93	0.844	1.008	Eq. (15) and (16) simplified. ($s=3.2 \times 10^{-8}$ cm.)
50	4.92	0.776	1.045	" " " " " "
90	3.76	0.707	1.023	" " " " " "
10	5.93	0.844	0.920	Eq. (15) and (16) ($s=5.0 \times 10^{-8}$ cm.)
50	4.92	0.776	0.973	" " " " " "
90	3.76	0.707	0.974	" " " " " "
Temp. Interval (°C.).				
10 to 50			0.282	Eq. (10 a).
50 to 90			2.921	" "
10 to 90			2.046	" "

$C=0.220$ is the average of two widely differing values calculated for the gas from data in Landolt-Börnstein, 4th edition. A large error in C has only a small effect upon the value of μ . The values of ϵ are obtained from P. Eversheim (*Ann. d. Phys.* xiii. p. 507 (1904)). D is calculated from the empirical equation, $D=1.328-0.00171T$. $s=3.2 \times 10^{-8}$ is calculated from the value of b given by Cardoso (*J. Chim. Phys.* x. p. 470 (1912)), and agrees well with the value 3.16×10^{-8} calculated from the mean collision area of the gas molecule given by A. O. Rankine and C. J. Smith (*Phil. Mag.* xlii. p. 615 (1921)). The calculations from the value $s=5.0 \times 10^{-8}$ are included to show the relatively small effect of a large error in the diameter upon the value of the electric moment.

No results are given in Table III. to show the effect of omitting the terms $\frac{3C^2}{2\pi}$ and $\frac{3M^2C^2}{2\pi^2N_0^2}$ from equations (15) and (16), although calculation shows the effect to be negligible. The values of μ for hydrogen sulphide agree well at the three different temperatures, which are remote from the freezing-point of the liquid. An increase of 56 per cent. in the value of s causes a decrease of only 7 per cent. in the value of the moment. The results calculated by means of equation (10 a) differ so widely as to be quite meaningless.

TABLE IV.

Chlorobenzene ($C = \cdot 2660$; $s = 4.82 \times 10^{-8}$ cm.).

Temp. ° C.	ϵ .	D.	$\mu \times 10^{18}$.	Method.
-20	6.93	1.149	1.207	Eq. (15) and (16) simplified.
"	"	"	1.259	Eq. (15) and (16).
0	6.42	1.128	1.289	" " " "
20	5.94	1.106	1.427	" " " "
100	4.70	1.019	1.418	" " " "

Bromobenzene ($C = \cdot 2079$; $s = 4.92 \times 10^{-8}$ cm.).

Temp. ° C.	ϵ .	D.	$\mu \times 10^{18}$.	Method.
-20	6.40	1.548	1.258	Eq. (15) and (16).
0	5.90	1.522	1.267	" " " "
20	5.53	1.495	1.286	" " " "
100	4.56	1.386	1.391	" " " "

For both substances, the values of the refractive indices and densities for calculation of C are obtained from Landolt-Börnstein, 4th edition. The values of ϵ and D are those given by Lertes (*loc. cit.*). s is calculated from the values of b obtained from the data of S. Young (*Sci. Proc. Roy. Dublin Soc. n. s. xii. p. 374 (1909-10)*).

The data on chlorobenzene and bromobenzene are tabulated together because of the similarity of these two substances.

For chlorobenzene, the effect of omitting the terms $\frac{3C^2}{2\pi}$ and $\frac{3M^2C^2}{2\pi^2N_0^2}$ is greater than in the case of ether or hydrogen sulphide, but is still small. The apparent value of μ for chlorobenzene, which freezes at -45° , increases with rise of temperature from -20° to $+20^\circ$, where it seems to become constant, while, for bromobenzene, which freezes at -30.5° , it is still rising at 20° , although it may be constant before 100° is reached. The lack of further data leaves this uncertain. The variation of the calculated values of μ with temperature is, however, not great, and seems to disappear altogether at temperatures well removed from the freezing-point of the liquid.

TABLE V.

Methyl Alcohol ($C = \cdot 250$; $s = 3\cdot 72 \times 10^{-8}$ cm.).

Temp. ° C.	ϵ .	D.	$\mu \times 10^{18}$.	Method.
-100	60.0	·9091	1.019	Eq. (15) and (16).
-70	51.5	·8787	1.142	" " " "
-40	44.0	·8503	1.234	" " " "
-10	37.5	·8217	1.336	" " " "
0	35.0	·8100	1.352	" " " "
20	31.2	·7915	1.434	" " " "
78.1	1.00745	·001112	1.931	Eq. (15) and (16) (Gas).
93.3	1.00655	·001066	1.855	" " " "
107.8	1.00589	·001025	1.799	" " " "
125.4	1.00531	·000980	1.777	" " " "
144.0	1.00476	·000936	1.756	" " " "
168.2	1.00449	·000885	1.795	" " " "
178.1	1.00431	·000866	1.809	" " " "

For the liquid, the values of ϵ are obtained from the measurements of R. Abegg and W. Seitz (*Zeits. Phys. Chem.* xxix. p. 242 (1899)), and the values of D from the work of W. Seitz, H. Alterthum, and G. Lechner (*Ann. d. Phys.* (4) xlix. p. 91 (1916), quoted by Isnardi (*loc. cit.*)) as well as from Landolt-Börnstein, 4th edition. For the gas, the values of ϵ are those given by M. Jona (*Phys. Zeits.* xx. p. 14 (1919)), and the densities are calculated on the assumption that the vapour behaves as an ideal gas, a procedure which is justifiable only because of the considerable errors probably occurring in the measurements of the dielectric constant.

The data on methyl alcohol are included because they cover the substance in both the liquid and the gaseous state. Unfortunately, a considerable gap in the data occurs between the liquid at 20° and the gas at $78^\circ 1$. The calculated value of μ for the liquid shows no approach to the constancy attained in the case of the other substances studied, but increases from the freezing-point almost as a linear function of the temperature. The value for the gas at $78^\circ 1$, which is only 12° above the boiling-point, is considerably higher than that for the liquid at 20° , but a small decrease occurs with rise of temperature. The very small increase which follows this decrease appears to be accidental, and may be attributed to small errors in the data. Indeed, one might be tempted to attribute all the variation in the value of μ for the gas to errors in the data, were it not that Jona's results point to a similar behaviour on the part of sulphur dioxide and water vapour in the neighbourhood of their boiling-points, and to a

smaller but similar effect in the case of ammonia, which was investigated at temperatures farther above the boiling-point. Jona explains the high value obtained for μ near the boiling-point as being due to molecular association, which alters the molecular concentration in this region, but becomes negligible at higher temperatures.

Of the liquids which have been discussed, only methyl alcohol is known to be strongly associated, and it is the only one which shows a steady increase in the apparent value of μ over the entire range of temperature in which it is investigated as a liquid. The apparent values of μ for the non-associated liquids generally show some increase as the temperature rises in the neighbourhood of the freezing-point, but soon attain constancy. The application of equations (15) and (16) to a crystalline or amorphous solid, in which the molecules are not free to move about, would lead to a calculated value of approximately zero for μ . In the immediate neighbourhood of the freezing-point of a liquid, the molecules, presumably, lack complete freedom of motion, because of the formation of aggregates, so that the values calculated for μ in this region of temperature might be expected to be low. As the temperature rises and this lack of freedom disappears, the calculated value of μ should approach the constant, true value. The effect of molecular association may be supposed to be similar to that produced by the molecular aggregation in the neighbourhood of the freezing-point—that is, lack of complete freedom of motion on the part of the molecules leads to calculated values of μ which are too low. As the degree of association decreases with rise of temperature, the calculated values of μ increase, reaching no constant value as long as association persists. In the gaseous state, where the intermolecular distances are large, the influence of association may be of quite another character, the predominating effect being, perhaps, that of change in concentration, as assumed by Jona, so that the alteration of μ with temperature in the gaseous condition may be altogether different from that in the liquid.

In equation (15) the values of s , M , and D are so increased by association that the term under the radical sign is somewhat decreased, and $\psi(\tau)$ may be considerably decreased because of the increase caused in the value of τ , as is evident from equation (16) and Table I. In the application of the equation to an associated liquid, no account is taken of the effect of association in increasing the values of s and M , which, because of our ignorance of the actual effect, are

treated as constants. The result is that the values of μ obtained in such calculations are smaller than the true ones, and approach the latter only as the true values of s and M approach the values used for them in the calculations. This would seem to explain the behaviour of the liquids when agglomeration in the neighbourhood of the freezing-point or association occurs.

The method of using the Gans equation suggested in this paper has another distinct advantage over that used by Isnardi and Gans in addition to its greater range of applicability. When applied to associated liquids the Isnardi and Gans method may lead to serious errors, which are minimized and detected by the present method.

This is made evident by a consideration of the two ways in which temperature affects the dielectric constant. Decreasing the temperature increases the dielectric constant by permitting increased alignment of the permanent doublets, and may also decrease the dielectric constant by increasing the degree of association—which latter effect is not taken account of in the equations. In strongly associated liquids this latter effect may nearly balance the former, so that the dielectric constant would show little variation with temperature.

In such cases the method of Isnardi and Gans would lead to the false conclusion that the molecular doublets possess very small moments. The present method would yield a value of the right order of magnitude, though too small, and would indicate the nature of the error by the failure of the calculated moment to take a constant value with increasing temperature.

Examples of this type of error may be cited. Isnardi finds that with carbon tetrachloride, carbon bisulphide, benzene and m-xylol, substances with very small electric

moments, $\frac{\epsilon - 1}{\epsilon + 2} \frac{1}{D}$ actually *decreases* with decreasing temperature, which would lead to an imaginary value for the moment if it were calculated from the value of ϵ at different temperatures. Again, with both methyl and ethyl alcohol $\frac{\epsilon - 1}{\epsilon + 2} \frac{1}{D}$ *decreases* with decreasing temperature, a circumstance which led Isnardi to class these substances with carbon tetrachloride, carbon bisulphide, benzene, and m-xylol as substances with practically no molecular electric moments. The present method, however, shows methyl and ethyl alcohol to have large electric moments, as is to be expected

from their strongly polar properties, and gives evidence of the effect of association which vitiates the older method. In the absence of complicating circumstances, such as association, the two methods should, of course, agree.

From these results, which have been selected as typical from among a considerable number of calculations, it may be concluded that equation (10 *a*), which resembles the Debye equation except for the presence of the factor $\frac{1}{D}$, cannot be

applied to liquids, although it should represent the behaviour of gases at high temperatures and low pressures. Equations (15) and (16) may be used to calculate the moments of the molecules of substances in both the liquid and the gaseous states, provided that there is no association or agglomeration of the molecules. This complication may be avoided in the case of non-associated liquids by working at temperatures considerably removed from the freezing-point. In the case of highly associated liquids, the true value of the moment of the single molecule is not given by equations (15) and (16), so that the substance must be studied in the gaseous condition. The fact that this method of calculation gives the value of the moment at a definite temperature, instead of the average value over a wide range, makes possible the detection of a variation with temperature, and hence of a change in the degree of molecular aggregation with temperature. It is thus possible to gain more accurate knowledge of the true values of the moments of many substances, and it is hoped that the application of these equations to associated liquids may throw some light upon the phenomena of association.

Some of the experimental aspects of this problem, which was originally suggested by Professor K. T. Compton, are being investigated in the Palmer Physical Laboratory with special apparatus made available through a grant from the Joseph Henry Fund of the National Academy of Sciences.

The writer wishes to acknowledge his deep indebtedness to Professor Compton for much helpful advice and criticism.

SUMMARY.

The simple form of equation proposed by Debye to represent the temperature variation of the dielectric constant of a substance cannot be used to calculate the electric moment from data upon the substance in the liquid condition.

A method is described whereby the electric moment of the molecule of a substance in the liquid or gaseous state may be

calculated from the indices of refraction at two different wave-lengths, the density of the substance under the conditions under which these indices are measured, the dielectric constant at one temperature, the density at this temperature, the molecular diameter, and certain universal constants.

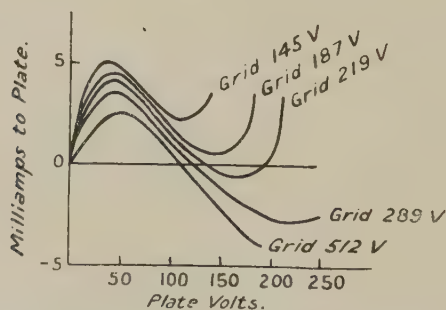
For normal liquids this method gives results in good agreement with those obtained by the method of Isnardi and Gans. For associated liquids, it leads to results which are low but which give an idea of the magnitude of the moment, while the method of Isnardi and Gans may lead to serious errors for such liquids.

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LXXXVIII. *The Emission of Secondary Electrons from Nickel.* By E. W. B. GILL, M.A., B.Sc., Fellow of Merton College, Oxford*.

1. **S**OME experiments recently made by Hull† on secondary emission, using a three-electrode valve at the lowest possible pressure, gave the results shown by the curves in fig. 1. In these experiments a stream of

Fig. 1.



electrons leave the hot filament whose potential may be taken as zero, and are attracted to the grid whose potential is $+V_G$; a proportion pass through and reach the plate whose potential is $+V_P$. The curves show the currents in the plate circuit for various values of V_P ; V_G being kept constant for each curve. So long as V_G is greater than V_P , any secondary electrons leaving the plate will be collected on

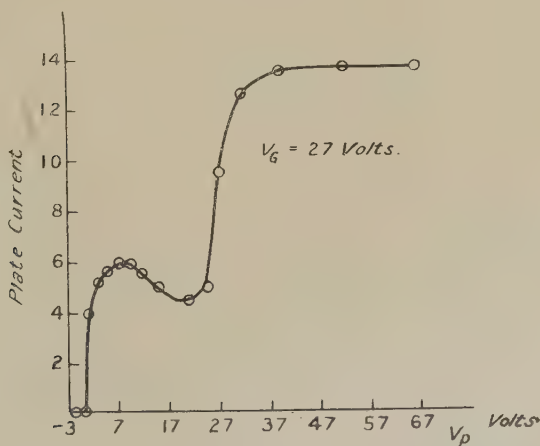
* Communicated by Prof. J. S. Townsend, F.R.S.

† Hull, Proc. Inst. Radio Engineers, Feb. 1918.

the grid, and the plate current correspondingly reduced. The velocity of impact on the plate of the primary electrons depends only on V_P , the total potential through which they fall after leaving the filament, and the increase of secondary emission with velocity of impact is shown by the downward slopes of the curves after V_P reaches the value of from 20 to 30 volts. Hull was chiefly interested in the application of these results to wireless telegraphy, the falling characteristic indicating instability and rendering it possible to use such an arrangement for the production of continuous oscillations or for the magnification of small potentials and currents; and I cannot find that he has given anywhere a detailed analysis of the curves.

Horton and Miss Davies* have also obtained a similar curve and put forward some explanations of it, but these explanations are not in agreement with the results of a series of experiments I have recently made.

Fig. 2.



They used plane and not cylindrical electrodes, the plate being of platinum. A slit was inserted between the filament and grid, and a magnetic force was applied perpendicular to the electrodes to keep the stream of electrons moving as far as possible in the same direction.

Their results are given by the curve (fig. 2) which, following the usual practice with valves, is plotted with the plate current through the valve indicated by ordinates

* Horton & Miss Davies, Proc. Roy. Soc. A. xcvii. p. 23 (1920).
Phil. Mag. Ser. 6. Vol. 45. No. 269. May 1923. 3 K

measured upwards. The abscissæ represent the plate potentials V_P , the grid being maintained constant at 27 volts.

As V_P increases, the various portions of the curve were explained as follows:—

- (A) The first rise is due to the electrons from the filament getting to the plate.
- (B) The nearly flat portion at the first maximum is due to the reflexion of the impacting electrons.
- (C) The drop is due to secondary emission of electrons whose excitation requires a minimum applied potential of from 10 to 11 volts and becomes of increasing importance as V_P increases.
- (D) After the minimum at about $V_P=20$ volts the number of secondary electrons leaving the plate decreases.
- (E) The final constant current which is attained at about 36 volts—that is, when the plate is 9 volts positive to the grid—indicates that the maximum velocity of the electrons leaving the plate is equivalent to that acquired by a fall through a potential difference of 9 volts.

These explanations will be considered later, but it may be remarked with regard to (B) that it does not appear that such experiments can discriminate between electrons which are reflected and secondary electrons emitted from the plate due to the impact of the primary stream. The proof that the whole phenomenon is not due to reflexion alone is that, as will be seen later, the number of electrons emitted from the plate can exceed the number that impinge on it, and the general smoothness of the curves renders it unlikely that at any point there is an abrupt transition from reflexion to emission; and as it is impossible by means of such experiments to distinguish emission from reflexion, all electrons receding from the plate will be referred to as secondary emission in this paper.

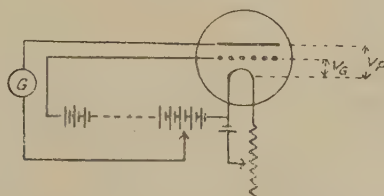
Some very recent work by Davisson and Kunsman* indicates that secondary emission occurs from nickel for values of V_P down to almost zero, and that these electrons are practically all emitted with low velocities, the number emitted with a high velocity being negligible. Their paper, however, is all contained in a short abstract of a few lines, and it is impossible to obtain details of their experiments.

* Davisson & Kunsman, *Phys. Rev.* 20, 1, p. 110.

The following experiments on secondary emission were made in order to obtain a satisfactory explanation of the anode currents under these conditions, and are interesting as emphasizing certain effects of grids which are now very largely used in determining critical potentials, and whose action in this connexion is not always sufficiently considered.

2. The experimental arrangements are shown by the diagram (fig. 3). The three-electrode valve used was a Marconi M.T. 5, described in detail in a recent paper (Phil. Mag., July 1922, p. 165), the vacuum being very low. The grid, and plate which was of nickel, were both cylindrical, the filament being along the axis. The grid was of square mesh of side about 1.5 mm. made of thin wire, the diameter of the grid and plate cylinders being 1 and 2.5 cms. respectively. The filament was heated to a dull red by a 2-volt accumulator with adjustable resistance in series.

Fig. 3.

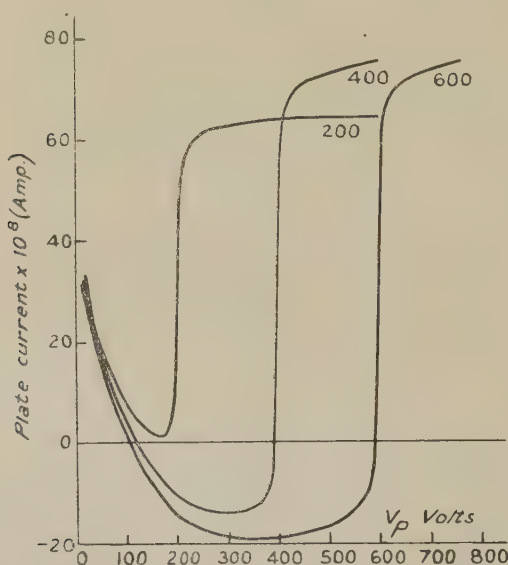


The grid was raised to a fixed potential V_G by a battery of small accumulators, and the plate maintained at various potentials V_P by the same accumulators. The negative pole of this battery was attached to the negative end of the filament, and in all cases V_G and V_P represent the potentials measured from this end. The voltage-drop down the filament was generally about 1 volt, and the potentials of grid and plate above the most active portion of the filament—the middle—are 5 volt less than V_G and V_P respectively. For the lower-plate voltages a potentiometer was used.

The plate currents were measured by a sensitive d'Arsonval galvanometer G . In some of the earlier experiments, resistances of about 50,000 ohms were inserted in both the plate and grid leads, as it was feared that the unstable characteristic would give rise to oscillations. Even with this resistance it was found that short-wave oscillations arose with the larger filament emissions, which were revealed by the galvanometer deflexion becoming unsteady, but with very low filament emissions there were no oscillations. In

the final experiments the resistances were not used, and the emission current did not exceed 10^{-6} ampere. It was found an advantage to connect the case of the galvanometer to one of the terminals, as otherwise for the higher potentials the electrostatic forces affected the moving coil. Three of the curves thus obtained connecting the plate current with the plate potential are given in fig. 4, the fixed grid potentials being 200, 400, and 600 volts respectively.

Fig. 4.



Unless the curves are drawn very large, the early parts are not easily distinguishable, and the first portions are therefore shown separately on a different scale and for a rather smaller emission in fig. 5.

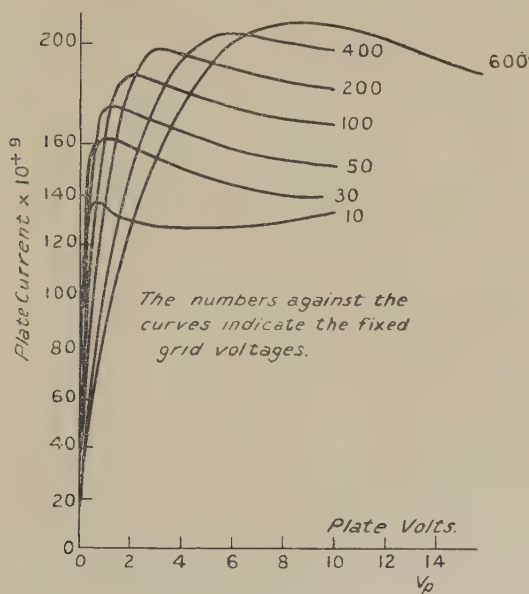
This last figure also contains the first part of curves corresponding to lower grid voltages from 100 to 10 volts. All the curves shown in fig. 5 were determined for me by Mr. C. W. Carter, Rhodes Scholar of Wadham College, Oxford.

It was noticed, as Hull had found, that an increase in the number of electrons leaving the filament over a reasonable range (provided that no oscillations occurred) merely increased the ordinates of all the curves in the same proportion. This is of importance as indicating that the

curves cannot be explained by a large saturation voltage being necessary between grid and plate to collect the secondary electrons on the grid.

3. All the curves taken on the above valve and others of various types showed the same general form as Hull's and Horton's. As V_P is increased from zero, there is a rapid rise in current to a maximum followed by a falling-off to a minimum, then a second rapid rise, and finally a slow

Fig. 5.



approach to a constant value. It will be noticed that the potential V_P which corresponds to the first maximum value of the plate current depends on the grid potential V_G , and increases as V_G is increased; also that the slope of the downward portions vary slightly, becoming steeper as V_G is increased, the successive curves dropping lower and lower. For V_G 400 and 600 the plate current reverses for certain ranges of V_P , showing that more electrons leave the plate than hit it. The final steep rise of current with V_P commences just before the plate potential reaches the same potential as the grid.

A separate experiment showed that any effects of radiation falling on the plate or of ionization of the trace of

residual gas were of the order of 10^{-6} of the effects measured, and are therefore negligible; and the downward bends of the curves can only be due to secondary emission, which in turn depends on the velocity of impact—*i. e.*, on V_P and not on V_G . It is necessary, therefore, to explain why it is that the curves do not, as might be expected, commence to bend down for the same values of V_P , whatever the value of V_G ; also as it is probable that in the experiments giving the curves in fig. 4 the number of primary electrons hitting the plate is approximately the same for the three values of V_G , it might be expected that the dropping portions of the curves should coincide, as the secondary emissions for a particular value of V_P should be the same.

Even if the numbers of electrons hitting the plate are not quite the same for the different values of V_G , it might be supposed that by multiplying the ordinates of one curve by a constant factor it would coincide with one of the other curves; but the figures plainly show this is not the case for the parts of the curves in question.

The discrepancy can be seen in another way. For $V_G=600$ the plate current is zero—that is, one impacting electron on the average sets free one secondary for a velocity given by $V_P=104$; and this is true for a considerable variation of the filament heating and consequent variation of the number of electrons impinging on the plate. For $V_G=400$ this equality is not obtained till $V_P=116$. Thus a marked difference is obtained where it might be supposed that the results would be the same.

4. A satisfactory explanation of the relative shapes of the curves may be obtained by considering the paths of the electrons in the valve. Omitting at first the complication due to the voltage drop down the filament and the distribution of velocities of emission from the filament consider the motion of a stream of electrons leaving the filament with zero velocity, the grid being at potential $+V_G$ and the filament and plate at zero potential. These electrons are accelerated up to the grid, where a portion are collected and the remainder pass through. After passing the grid the force on them is reversed, and if they all moved in straight lines they would just reach the plate with zero velocity. In actual practice the paths are not straight, for as they pass through the grid-spaces they get bent to varying degrees. The force near the very thin grid wires is comparatively large, and the electrons passing through this region are

considerably deflected, while the few which pass through the centre of the grid opening are undeflected.

The retarding force acting on the electrons after they pass the grid bends their paths more and more, with the result that they nearly all return to the grid along curved paths. At the point on their orbit which is furthest from the grid—that is, the turning point—they still have velocity; and if for a particular electron this velocity is equivalent to that due to a fall through a potential difference v_0 , the electron gets as far as the equipotential surface v_0 , and would require a superposed potential v_0 to take it to the plate.

The electrons thus turn at various distances from the plate, those which passed nearest to the grid wires turning at the furthest distance from the plate. Let v be the potential at the points where the latter begin to return to the plate. If the plate potential be gradually raised from zero, the number of electrons reaching the plate will increase rapidly at first, and then slower and slower till the plate potential reaches v , when the plate receives all the electrons which enter the space between the grid and the plate.

After attaining the potential v , the number of electrons reaching the plate remains constant for a considerable increase of V_P above this value.

The actual value of this voltage v depends on V_G ; and, although there is no exact proportionality, it is obvious that if V_G is increased, v is also increased, and a larger voltage is necessary to bring all the electrons to the plate.

Thus the primary current to the plate through the valve for a fixed grid potential rises from zero to a saturation value as V_P is increased from zero to v ; the value of v at which the current becomes constant is dependent on V_G being increased if V_G is increased. This primary current is, however, not shown by the curves obtained in practice, as it is only possible to measure the net current received by the plate—*i. e.*, the primary current less any secondary emission current.

The result of these considerations can be best seen by a study of the curves of fig. 5.

For a low value of the grid voltage such as 10 volts a small value of V_P , probably about 1 volt, is sufficient to cause all the electrons which pass through the grid to reach the plate. A further increase of V_P does not affect the number which reach the plate; and hence, if there were no secondary emission, the current should remain constant when V_P is increased above about 1 volt.

The current in actual fact begins to decrease, and for 1.5 volts is less than for 1 volt, indicating that secondary emission has become appreciable when the primary electron falls through 1.5 volts. The number of secondaries is here only a small fraction of the number of primaries.

This curve thus proves that secondary electrons are being given off for $V_P=1.5$ volts; and as the emission depends only on the velocity of impact, there must be a secondary emission for $V_P=1.5$ whatever the value of V_G .

The plate currents for the higher values of V_G do not, however, show any signs of decreasing just after V_P reaches 1 volt. Thus for $V_G=100$ the current increases till $V_P=2$, for $V_G=400$ till $V_P=6$, and for $V_G=600$ till $V_P=9$.

In all these cases the secondary emission which we know exists for $V_P=1.5$ does not reveal itself in the curve, because for the larger grid voltages $V_P=1.5$ does not bring all the primary electrons which passed the grid to the plate.

Thus as V_P is increased beyond 1.5, more primaries reach the plate, and the current continues to grow because the increase in the number of primaries collected more than compensates for the secondaries leaving the plate. The experiments show that as V_G is increased, the value of V_P necessary to bring all the primaries to the plate is also increased.

The argument of Horton and Miss Davies that because, with their particular grid voltage, the plate current did not decrease till V_P reached 11 volts therefore secondary emission requires the primary to have a minimum voltage drop of 11, is plainly incorrect as it is impossible to maintain that secondary emission only begins when the plate current begins to decrease.

It is also impossible to maintain that just before 11 volts electrons are reflected from the plate as indicated by the "nearly flat portion of the curve," for each curve in fig. 5 has a nearly flat portion, each for different ranges of V_P .

The general idea that the primary stream is undeflected in passing through a grid of fine mesh is erroneous, especially as a fine mesh is generally composed of very fine wire. This was confirmed by some experiments with another Marconi valve in which the grid had a much finer mesh. With this valve for $V_G=200$ the plate potential at which the current began to diminish was about 8 volts as compared with 3 volts for the M.T. 5 valve with which the curves in fig. 5 were obtained. It might also be remarked that the curving of the paths of the electrons and the phenomena

resulting therefrom will not be eliminated by increasing the number of grids or by putting in slits near the filament.

The voltage drop down the filament, the distribution of the velocities of the electrons emitted from the filament about their mean values, and contact differences of potential do not affect the general form of the curves to be expected from the simple theory; but it would be necessary to take these effects into consideration in order to estimate the lowest potentials at which the various phenomena may begin to be noticeable.

5. The slight difference in the shapes of the various curves over the portions where the plate current diminishes as the plate potential increases may also be explained by considering the curvature of the paths of the electrons.

Over this region all the primary electrons passing the grid hit the plate. For any particular value of V_G as V_P is increased the retarding force on the electrons after they have passed the grid decreases, which means that the average incidence of the electrons on the plate is most oblique for the low values of V_P and becomes more normal as V_P is increased. To compare the different curves it is best, however, to consider a fixed velocity of impact, that is a fixed value of the plate potential, when by calculating mathematically the effect of varying V_G it can be shown that the higher the value of V_G the more oblique the incidence.

This last fact affords a clue to the apparent non-correspondence of the curves. It has been known for a long time that the number of secondary electrons emitted depends on the angle of incidence of the primary electrons * being a minimum for normal incidence and increasing at any rate initially as the angle becomes more oblique. Thus as V_P is increased, we should expect the curve for $V_G=400$ to drop more steeply than that for $V_G=200$, since an increase of V_P leaves the incidence more oblique in the first than in the second, and the emission thus increases more for the first than for the second. The curves agree with this. Or, if it is preferable to study the points where the curves cut the V_P axis, agreement is also found.

Thus for $V_G=400$ if $V_P=116$, each primary electron which hits the plate with a velocity corresponding to a drop through 116 volts on the average produces one secondary. For $V_G=600$ and more oblique incidence, if $V_P=116$ each primary on the average produces more than one secondary, and V_P need only be 104 to get an average of one. Higher

* *Electricity in Gases*, p. 457 (1915).

values of V_G reduce the value of V_P necessary for equality of incidence and emission still further.

6. The final rise of the curves when V_P approaches the value of V_G indicates that the effect of secondary emission is becoming less. This does not mean that the number of secondaries given off decreases, but that the number of them which reach the grid decreases. Thus in fig. 4 when $V_G=200$ the curve rises after V_P reaches 170 approximately, but the other curves for $V_G=400$ and 600 show that as V_P is increased from 170 to 200 the emission also increases, and the rise of the curve for $V_G=200$ can therefore only be due to some of the secondary electrons returning to the plate and not escaping to the grid; the proportion returning increasing as V_P is increased till, for the higher values of V_P , they all return, and secondary emission has no effect. The simple idea underlying the explanation of Horton and Miss Davies that the field between the grid and the plate is determined solely by the potentials of the grid and the plate, is quite unable to explain this rise; for in all cases the rise begins when V_P is *less* than V_G —that is, when the field, if due to V_G and V_P alone, would certainly remove the secondary electrons to the grid. (Careful experiments with widely varying currents showed that it is only when V_P is very close in value to V_G that the space-charge round the plate has any appreciable effect.)

The difficulty about the early rise is evaded by Horton and Miss Davies, who remark about the rise in their curve after $V_P=22$ (V_G being 27) that this “indicates that the number of electrons leaving the collecting electrode begins to decrease, causing the resultant negative current to increase,” no reason being given why the number leaving does not decrease. The solution of the difficulty is to be found by a more careful examination of the electric fields.

Starting with the case when the plate and filament are both at zero potential and the grid is at potential V_G , the potential at points in the grid squares drops off as we leave the grid wires, and gets to a minimum at the centre of the square.

It is not necessary for present purposes to attempt the calculation of the variation of the potential across the grid spaces for cylindrical electrodes and grid wires of circular cross-section, but it appears that owing to the large force just outside thin charged wires this variation may be considerable.

Thus when the filament and plate are at zero potential and

the grid at potential V_G , the field is not uniform near the grid, but it is uniform near the plate.

If the plate potential V_P is now raised, V_G being fixed, the field near the plate weakens *, and a mathematical investigation shows that this field becomes zero and reverses for values of V_P less than V_G .

This can also be seen as follows :—When V_P and V_G are equal and the filament is at zero potential, the majority of the lines of force leaving the filament go to the grid, but a few go to the plate ; no others exist, as none can go from the grid to the plate, and hence the force near the plate attracts electrons to it. Hence a reversal must take place before the plate potential becomes equal to that of the grid.

The secondary electrons are emitted with small velocities of various magnitudes ; and therefore as the attractive force on electrons at the surface of the plate increases with V_P , less and less of them get free from the plate, so that the plate current begins to increase a little before V_P reaches the same value as V_G . The secondary emission finally has no effect on the plate current when V_P reaches such a value that the field prevents the fastest secondaries leaving the plate.

The final value to which the plate current approaches as V_P is increased depends on another factor. It will be noticed that the final value of the plate current obtained by increasing V_P is considerably larger than the plate current at its first maximum.

But the current at the first maximum is very approximately equal to the current carried by all the electrons which pass through the grid for the particular value of V_P which gives this maximum since the secondary effect for these low voltages is small.

It is thus evident that as V_P is increased, the proportion of the electrons leaving the filament which pass through the grid increases—that is, the primary current to the plate increases at the expense of the primary current to the grid. (This, of course, could not be the case if it were assumed that the grid acts as a perfect shield and the potential of the plate has no effect on the field between filament and grid.)

Apart, therefore, from any effect of secondary emission, the growth of the plate current as V_P is increased depends on the rate at which the plate robs the grid of its current, and this depends on the dimensions of the parts of the valve.

* The equipotentials for a similar case were worked out by Maxwell (*Electricity and Magnetism*, vol. 1. Art. 203 and fig. xiii.).

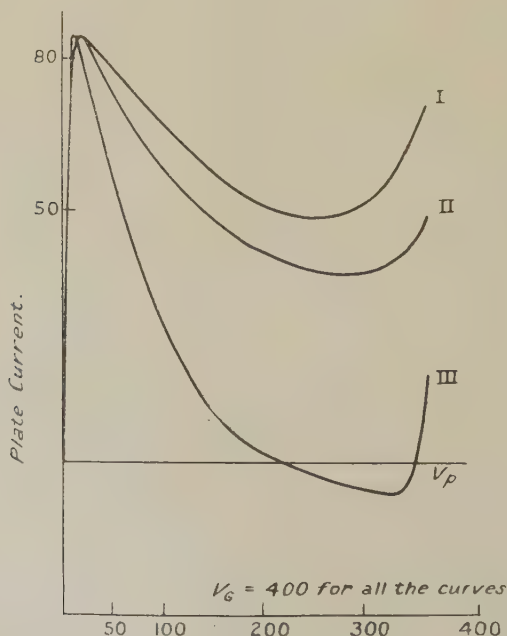
The shape of the curve for the larger values of V_P depends, therefore, both on the elimination of the effect of secondary emission and the diminution of the grid current.

Horton and Miss Davies only allowed for the former in their explanation of this part of the curve, and their estimate of 9 volts as the equivalent velocity of emission of the fastest secondary electron is therefore unreliable, and its agreement with the results of Lenard and others must have been accidental.

It is somewhat difficult to state the values of the plate potentials for which the curves shown in fig. 4 may be said to attain saturation, but these potentials are certainly more than 20 volts above the corresponding grid potentials.

7. The importance of the angle of impact upon the emission is well shown in the curves of fig. 6, which

Fig. 6.



represent the curves taken on three valves—I, II, and III, V_G being 400 for each. These valves were larger than the M.T. 5 valve, and were all very similar in dimensions, except

that the plate of III, though a cylinder of the same average diameter as I and II, was corrugated. The electrons would thus on the average hit the plate of III at a more oblique angle than in I and II. (The grids of these valves were very open, so that in I and II the majority of impacts were nearly normal and the emission less than in fig. 4.)

The currents were measured with both the valves I and II to make certain that small differences in the dimensions of two similar valves did not affect the curves very much.

Curve III shows the much higher emission from the corrugated plate.

8. The explanations given appear to be in satisfactory agreement with the experiments, and the general conclusions may be stated as follows :—

When V_G is large and V_P small, the filament being at zero, it is legitimate to regard the spaces from filament to grid and from grid to plate as being two independent fields; the first determined by the potential difference between filament and grid, the second by that between grid and plate. The electrons entering this latter space enter at various (small) angles to the normal at the point of entry, and the retarding force causes them to move in curved orbits. There are two consequences of this: the first that V_P must reach a certain value before all the primary electrons hit the plate, which causes the plate current to increase with V_P for a bit after secondary emission has commenced; the second that the electrons hit the plate at various angles. The magnitude of both of these effects depends on V_G in a way which can be qualitatively but not quantitatively estimated.

As V_P is further increased, the secondary emission depends not only on the velocity of impact, *i. e.* on V_P , but also on the angle of impact which depends on V_G .

Other considerations come in when V_P approaches V_G in value, and there is very considerable interpenetration of the fields on the two sides of the grid. The field near the plate reverses, and tends to stop the escape of secondary electrons before V_P attains the value of V_G . The effect of secondary emission begins to decrease from this point till, when V_P is sufficiently high above V_G , the velocities of emission of the secondary electrons are not sufficient to prevent them returning to the plate, and secondary emission has no effect on the plate current. It is not, however, possible to determine accurately the point at which the effect of

secondary emission becomes negligible, as the growth of the plate current with increasing V_P is also influenced by electrons which for lower values of V_P went direct from the filament to the grid, being diverted from the grid to the plate.

Owing, therefore, to the number of primary electrons reaching the plate for any value of V_P not being accurately known, and as moreover the angles at which they hit the plate cannot be determined, the curves do not give any precise measurements of the magnitude of secondary emission for definite velocities and angles of impact.

They do show roughly, however, that as the velocity of impact is increased, the number of secondaries emitted for a given number of primaries increases with the velocity of impact, and that the increase continues further if the impact is made more oblique.

The velocity of impact at which secondary emission first became apparent is reduced by reducing V_G ; and even allowing for the velocity of emission of the primary from the filament and contact differences of potential, it seems that there is secondary emission (or reflexion) when the primary drops through one volt or less.

I am indebted to Mr. F. B. Pidduck for some information concerning the electrostatic fields, and to Professor Townsend, in whose laboratory the experiments were made, for much useful advice and criticism.

Note.—The variation of potential over the grid spaces referred to in paragraph 6 appears to have been overlooked by certain experimenters: and a variation will still exist however many grids are employed, and it is not easy to see the validity of the claim sometimes made to fix ionizing and radiating potentials to $\frac{1}{100}$ of a volt when the electrons producing the effect pass through a grid. These values are obtained from the grid potentials as if all the electrons passed through an identical field, whereas, in fact, the majority of them pass the grid at points whose potential certainly differs from that of the grid by more than $\frac{1}{100}$ of a volt.

LXXXIX. *On Ionic Oscillations in the Striated Glow Discharge.* By E. V. APPLETON, M.A., D.Sc., and A. G. D. WEST, B.A., B.Sc., Denman Baynes Research Student, Clare College, Cambridge*.

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IN the course of some experiments on the electrical properties of ionized gases for high-frequency electromotive forces, it was found that the ordinary striated glow discharge was more often than not a generator of electric waves. The production of such waves indicates that the discharge is not steady, as is usually supposed, but is actually pulsating in character. The presence of the waves may be detected by the ordinary wireless receiving devices, and most conveniently by an auto-heterodyne triode receiver, by means of which it may be shown that the frequency of the oscillations is independent of the electrical constants of the circuit external to the discharge-tube.

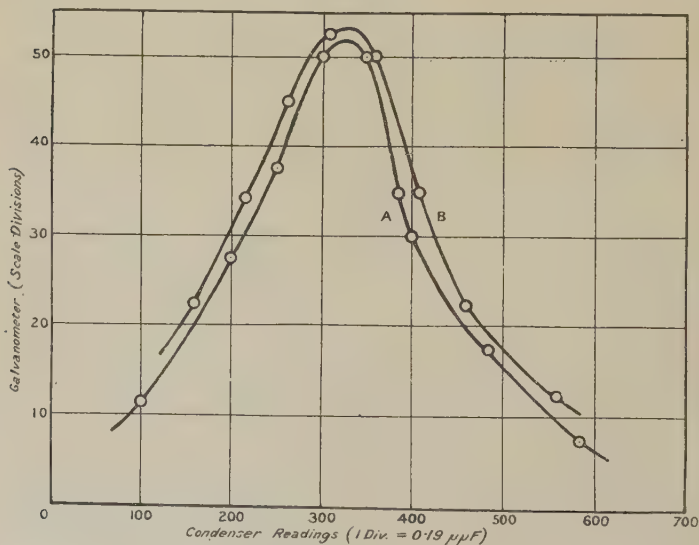
The discharge-tube used was of the simplest type, the diameter being 3.7 cm. and the distance between the electrodes 22 cm. The cathode used in the first instance was of heated platinum (lime-coated), though later experiments showed that a cold cathode will answer quite as well. When a hot cathode was used the anode potential was normally 80–120 volts, but this was increased to 600–800 volts in the case of a cold cathode. In both cases the discharge had to be started by an induction-coil. The anode current was usually of the order of a few milliamperes. When a hot cathode was used the pressure in the discharge-tube was about 0.005 mm. of mercury, but this was increased to 0.25 mm. when the cathode was cold. The number of striations in the tube was adjusted either by altering the gas-pressure or anode potential or by drawing out the striations with a magnet. Oscillations seemed to be most easily obtained when the induction-coil discharge had continued for some time before the steady anode potential was applied. Their production also seemed to depend in some way on the presence of a small glow at the surface of the anode. A noticeable flickering of this glow was found to accompany instability of the discharge.

The ionic oscillations have been detected in three ways, each of which seems to have certain points of interest. In the first method a condenser consisting of two curved tin-foil plates was attached to the outside of the discharge-tube, and also connected in parallel with the condenser of an

* Communicated by Prof. Sir E. Rutherford, F.R.S.

auto-heterodyne receiver. Combination tones of the usual type were heard when the triode-receiver frequency was sufficiently near the frequency of the ionic oscillations of the discharge. The various harmonics of the ionic oscillations were also observed and identified. It was, however, noticed that the note of the combination tone was often not as pure as that heard in the reception of continuous waves from arc or triode generators. In cases when the note was not pure the effect in the telephone can perhaps best be described as being similar to a continuous-wave signal superposed on a background of "atmospherics." Such impurities in the combination tone led us to adopt the second method of detection, in the hope of ascertaining how far from sinusoidal the oscillations were. An oscillatory circuit was fitted up with a diode rectifier and galvanometer

Fig. 1.



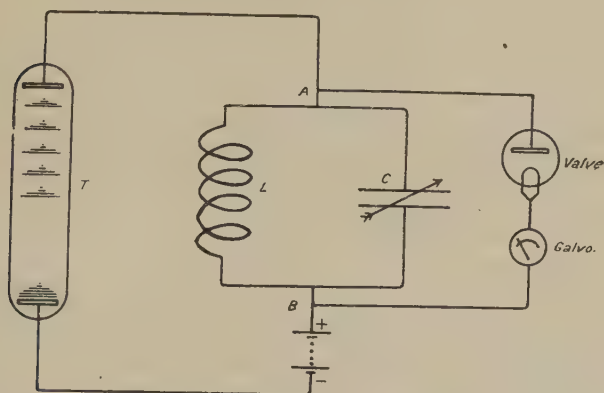
connected in series across the condenser, and the whole placed close to the discharge-tube. A "resonance curve" was obtained for the ionic oscillations and compared with that for a sine-wave generator (triode). These curves are shown as A and B respectively in fig. 1, and it is evident from their similarity that the minor discharges which give rise to the "atmospherics" mentioned above are small compared with the main continuous oscillation.

It is of interest to ascertain whether this method of generating electric waves is to be classed with any of the

known methods. At first sight an analogy with the arc or dynatron is suggested, but it was found that the frequency of the discharge-tube oscillations was independent of the electrical constants of the external circuit. The oscillations are therefore of a new type, being ionic in character and origin.

To illustrate the fact that the frequency of the oscillations was uniquely determined by the internal characteristics of the discharge, an oscillatory circuit was introduced in the anode circuit of the tube, as shown in fig. 2. A diode

Fig. 2.



and galvanometer were used for detecting any oscillatory potential between the points A and B. On gradually increasing the capacity, it was found that for one particular value a large deflexion of the galvanometer was obtained. It is obvious that this happened when the oscillatory circuit LC resonated to the frequency of the oscillations generated in the discharge. Usually the frequencies were of the order of 10^5 per second corresponding to wave-lengths of 2000 to 4000 metres, but in isolated cases frequencies as low as 10^3 have been observed.

In the particular tube we used, the conditions most favourable for the production of oscillations were those in which three or four complete striations were present. We have not made a detailed examination of the dependence of frequency on gas-pressure and anode potential, but have noted that the frequency usually increases with increase of pressure and also with increase of anode potential.

Cavendish Laboratory, Cambridge.
December 1922.

XC. *An Investigation of the Structure of the Halogen Salts based on their Compressibility.* By IDA WOODWARD*.

THE halogen salts crystallize in the cubic system, the atoms of the alkali metals and those of the halogens being arranged alternately at the corners of the cubes. The following calculations are based on the hypothesis (Sir J. J. Thomson, *Phil. Mag.* Oct. 1922, p. 662) that the octet of the halogen is completed by the single electron from the outermost shell of the alkali, and that these eight electrons lie at the corners of a cube, which from considerations of symmetry has its edges parallel to those of the cube of the crystal lattice.

Let a be the distance between two adjacent atoms, and $2y$ the edge of the cube of electrons. Then the potential energy per unit volume is a function of a and y , say $f(a, y)$. The condition for the equilibrium of the system is that $f(a, y)$ shall be a minimum for small changes in a and y .

$$\text{That is,} \quad \frac{\partial f}{\partial a} = 0 \quad \text{and} \quad \frac{\partial f}{\partial y} = 0.$$

$$\text{Hence} \quad \frac{df}{da} = \frac{\partial f}{\partial a} + \frac{dy}{da} \cdot \frac{\partial f}{\partial y} = 0.$$

Now the work required per unit volume to compress the crystal so that a is changed to $a - \Delta a$ is

$$\begin{aligned} \frac{df}{da} \cdot \Delta a + \frac{1}{2} \cdot \frac{d^2f}{da^2} \cdot (\Delta a)^2 + \dots \\ = \frac{1}{2} \cdot \frac{d^2f}{da^2} \cdot (\Delta a)^2 + \dots \end{aligned}$$

If this changes a volume V to $V - \Delta V$, and C is the compressibility, the work done per unit volume is

$$\frac{1}{2} \cdot \frac{1}{C} \cdot \left(\frac{\Delta V}{V} \right)^2.$$

It is therefore necessary to calculate $\frac{d^2f}{da^2}$. It will be shown, however, that $\frac{dy}{da}$ is small, so that $\frac{\partial^2 f}{\partial a^2}$ may be substituted for $\frac{d^2f}{da^2}$ without introducing a large error, since

$$\frac{d^2f}{da^2} = \frac{\partial^2 f}{\partial a^2} + 2 \cdot \frac{dy}{da} \cdot \frac{\partial^2 f}{\partial y \partial a} + \left(\frac{dy}{da} \right)^2 \cdot \frac{\partial^2 f}{\partial y^2}.$$

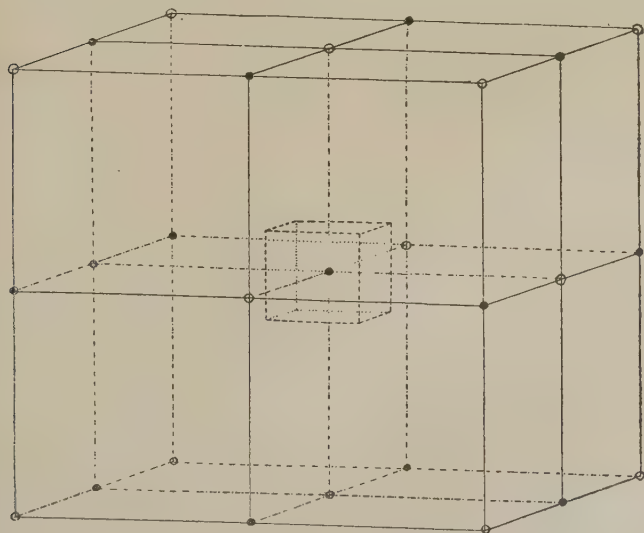
* Communicated by Sir J. J. Thomson, O.M., F.R.S.

The forces acting are assumed to be :

- (i.) a repulsion $\frac{e^2}{r^2}$ between electrons ;
- (ii.) an attraction $\frac{eE}{r^2}$ between a halogen atom and an electron other than those of its own shell ;
- (iii.) an attraction $eE\left(\frac{1}{r^2} - \frac{d}{r^3}\right)$ between a halogen atom and an electron of its own shell ;
- (iv.) an attraction $eE\left(\frac{1}{r^2} - \frac{c}{r^3}\right)$ between an alkali atom and an electron ;
- (v.) a repulsion $EE'\left(\frac{1}{r^2} - \frac{g}{r^3}\right)$ between two atoms ;

where d , c , and g are constants depending on the elements concerned.

Fig. 1.



The diagram (fig. 1) shows a cube of edge $2a$. Halogen atoms lie at the centre of this cube and at the middle points

of the edges. Alkali atoms lie at the corners and at the centres of the faces. The electrons lie at the corners of cubes of edge $2y$ surrounding the halogen atoms. Only one of these cubes is shown in the diagram.

Now, an approximation to the potential energy of the halogen atom lying at the centre of the cube of edge $2a$ is obtained by considering the contribution due to the atoms shown and to the electrons which lie within the cube. Since the atoms at the corners are shared by eight cubes, those at the middle points of the edges by four, and those at the centres of the faces by two, this contribution is

$$\frac{1}{2} \cdot 7e \left\{ 8 \cdot \frac{e}{\sqrt{3}a} + \frac{6}{2} \cdot \frac{e}{a} + \frac{12}{4} \cdot \frac{7e}{\sqrt{2}a} - \frac{G}{a^2} - \frac{8e}{\sqrt{3}y} + \frac{4de}{3y^2} - \frac{24e}{\sqrt{2(a-y)^2 + y^2}} \right\},$$

where $\frac{G}{a^2}$ includes the terms arising from the r^{-3} forces between atoms.

If similar cubes are drawn surrounding an alkali atom and an electron respectively, and the potential energy of these is calculated, it is found that the potential energy of a group consisting of one halogen atom, one alkali atom, and eight electrons is

$$e^2 \times \left[\begin{aligned} & \frac{86 \cdot 568}{a} - \frac{B}{a^2} - \frac{20 \cdot 9364}{y} + \frac{9 \cdot 333}{y^2} \cdot d - \frac{4 \cdot 6192}{a-y} \\ & + \frac{1 \cdot 333c}{(a-y)^2} + \frac{8 \cdot 4864}{a-2y} \\ & + 12 \left\{ \frac{1}{\sqrt{2a^2 + 4y^2}} + \frac{2}{\sqrt{2a^2 + 4ay + 4y^2}} \right. \\ & \quad \left. + \frac{2}{\sqrt{2a^2 - 4ay + 8y^2}} + \frac{1}{\sqrt{2a^2 - 8ay + 12y^2}} \right\} \\ & - \frac{168}{\sqrt{2a^2 - 4ay + 3y^2}} - \frac{24}{\sqrt{a^2 - 2ay + 3y^2}} \\ & \quad + \frac{12c}{a^2 - 2ay + 3y^2} \end{aligned} \right] \\ = U \text{ (say), } \dots \dots \dots \text{ (I.)}$$

where B is a constant.

So that $N \cdot U = f(a, y)$, where N is the number of groups per unit volume.

Since the cube of electrons is in equilibrium, $\frac{\partial U}{\partial y} = 0$.
Hence

$$\frac{e^2}{a^2} \times \left[\begin{aligned} & \frac{20.9364}{x^2} - \frac{18.667}{x^3} \cdot \frac{d}{a} \cdot \frac{4.6192}{(1-x)^2} \\ & + \frac{2.667}{(1-x)^3} \cdot \frac{c}{a} + \frac{16.9728}{(1-2x)^2} \\ & + 12 \left\{ \frac{-4x}{(2+4x^2)^{3/2}} + \frac{2(2-4x)}{(2-4x+4x^2)^{3/2}} \right. \\ & \quad \left. + \frac{2(2-8x)}{(2-4x+8x^2)^{3/2}} + \frac{4-12x}{(2-8x+12x^2)^{3/2}} \right\} \\ & - \frac{168(2-3x)}{(2-4x+3x^2)^{3/2}} - \frac{24(1-3x)}{(1-2x+3x^2)^{3/2}} \\ & \quad + \frac{12(2-6x)c}{(1-2x+3x^2)^2} \end{aligned} \right] \\ = 0, \dots \dots \dots (II.)$$

where $x=y/a$.

If we evaluate the expression on the left-hand side of this equation for different values of x , we obtain the following set of corresponding values of x , $\frac{d}{a}$, and y .

TABLE I.

x .	d/a .	y .
0	0	
·05	·0554	$d/1.11$
·075	·082	$d/1.09$
·1	·108	$d/1.08$
·125	·131+·003 c/a	$(d-·003 c)/1.05$
·2	·187+·010 c/a	$(d-·010 c)/·93$
·25	·213+·016 c/a	$(d-·016 c)/·852$
·3	·255+·011 c/a	$(d-·011 c)/·85$

Hence the variation of y with x , and therefore with a , is small, and in calculating the compressibility from $\frac{\partial^2 U}{\partial a^2}$ instead of $\frac{d^2 U}{da^2}$, we shall not be introducing a large error.

Putting $\frac{\partial U}{\partial a} = 0$, since the system is in equilibrium, and eliminating B by means of this equation, we get

$$\frac{\partial^2 U}{\partial a^2} = \frac{e^2}{a^3} \times \left[\begin{aligned} & -86.568 + \frac{13.857}{(1-x)^2} - \frac{9.238}{(1-x)^3} \\ & - \frac{8c}{(1-x)^3 a} + \frac{8c}{(1-x)^4 a} - \frac{25.459}{(1-2x)^2} \\ & + \frac{16.973}{(1-2x)^3} + \frac{336(4-3x)}{(2-4x+3x^2)^{3/2}} \\ & - \frac{504(2-2x)^2}{(2-4x+3x^2)^{5/2}} + \frac{24(4-3x)}{(1-2x+3x^2)^{3/2}} \\ & - \frac{72(1-x)^2}{(1-2x+3x^2)^{5/2}} - \frac{24(4-3x)}{(1-2x+3x^2)^2} \cdot \frac{c}{a} \\ & + \frac{24(2-2x)^2}{(1-2x+3x^2)^3} \cdot \frac{c}{a} \\ & + 12 \left\{ \frac{-8}{(2+4x^2)^{3/2}} - \frac{4(4-3x)}{(2-4x+4x^2)^{3/2}} \right. \\ & - \frac{4(4-3x)}{(2-4x+8x^2)^{3/2}} - \frac{2(4-6x)}{(2-8x+12x^2)^{3/2}} \\ & + \frac{12}{(2+4x^2)^{5/2}} + \frac{24(1-x)^2}{(2-4x+4x^2)^{5/2}} \\ & \left. + \frac{24(1-x)^2}{(2-4x+8x^2)^{5/2}} + \frac{12(1-2x)^2}{(2-8x+12x^2)^{5/2}} \right\} \end{aligned} \right] \\ = \frac{e^2}{a^3} \times A \text{ (say).}$$

The following table gives the value of A for various values of x :—

TABLE II.

x .	A.
0	1.456
.05	0.77 + 4.29 c/a
.075	0.5 + 6.42 c/a
.1	0.29 + 8.29 c/a
.125	0.58 + 9.91 c/a
.2	3.07 + 11.1 c/a
.25	17.2 + 7.42 c/a
.3	73.26 + 0.59 c/a

Employing the method given by Prof. Sir J. J. Thomson (Phil. Mag. April 1922, p. 735) it is found that the work required to compress N groups of 1 halogen atom, 1 alkali atom, and 8 electrons is

$$\frac{1}{2} \cdot N \cdot \frac{A}{9} \cdot \frac{e^2}{a} \cdot \left(\frac{\Delta V}{V} \right)^2,$$

where V is the volume occupied by the N groups. Also if C be the compressibility, the work done per unit volume

$$= \frac{1}{2} \cdot \frac{1}{C} \cdot \left(\frac{\Delta V}{V} \right)^2.$$

Hence
$$A = \frac{9a}{CN e^2},$$

where N is now the number of groups per unit volume.

If M is the mass of one group and Δ the density, $NM = \Delta$ and $N \cdot 2a^3 = 1$.

Therefore
$$A = \frac{9}{e^2 \cdot C \cdot (2)^{1/3}} \cdot \left(\frac{M}{\Delta} \right)^{4/3}.$$

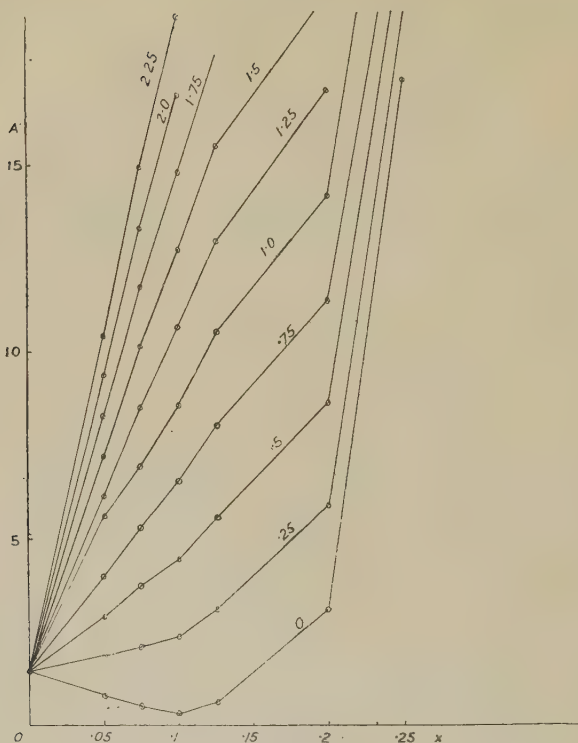
The values of A , calculated from the experimental values for the compressibilities of the six following salts (T. W. Richards and G. Jones, Journ. Am. Chem. Soc. xxxi. p. 176), are:

	NaCl.	NaBr.	NaI.	KCl.	KBr.	KI.
A.....	12.32	12.45	12.75	15.61	15.27	14.41

We have to find values of c for Na and K, and values of d for Cl, Br, and I, such that A has the above values for the various salts.

Consider NaCl. From Table II. graphs of (A, x) for different values of c/a were drawn (fig. 2). The intersections of these curves with the line $A=12.32$ give a set of corresponding values of x and c/a shown in the first two rows of the table below. From the second column of Table I. graphs of $(d/a, x)$ for the same set of values of c/a were also

Fig. 2.

Graph of (A, x) for different values of c/a .

drawn (fig. 3), and from this a set of corresponding values of d/a was determined, as shown in the third row of the table.

$c/a \dots$	0	.25	.5	.75	1.0	1.25	1.5	1.75	2.0	2.25
$x \dots\dots$.231	.222	.213	.204	.161	.118	.095	.079	.068	.060
$d/a \dots$.203	.202	.200	.197	.165	.127	.103	.086	.075	.065

For NaCl, $a = 2.817 \text{ \AA}$; so we get the following set of corresponding values of c and d (fig. 4) in Ångström units:—

$c \dots$	0	.704	1.408	2.113	2.817	3.521	4.225	4.930	5.634	6.338
$d \dots$.5719	.5691	.5634	.5550	.4646	.3577	.2901	.2424	.2141	.1831

Fig. 3.

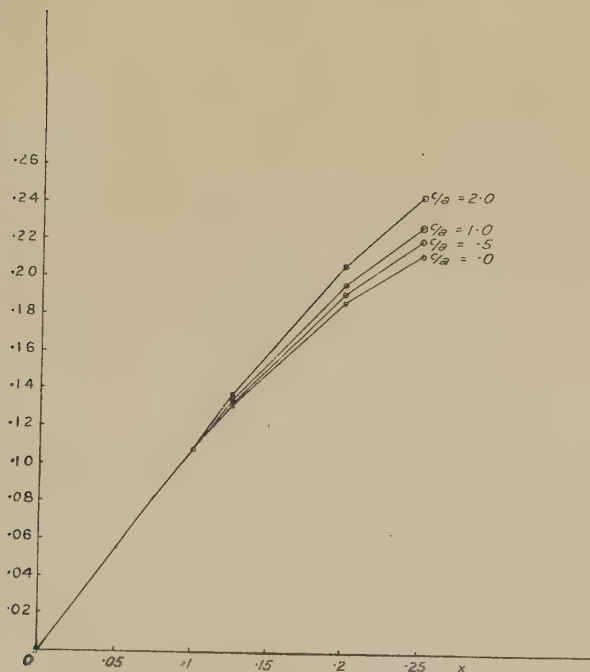
Graph of $(d/a, x)$ for different values of c/a .

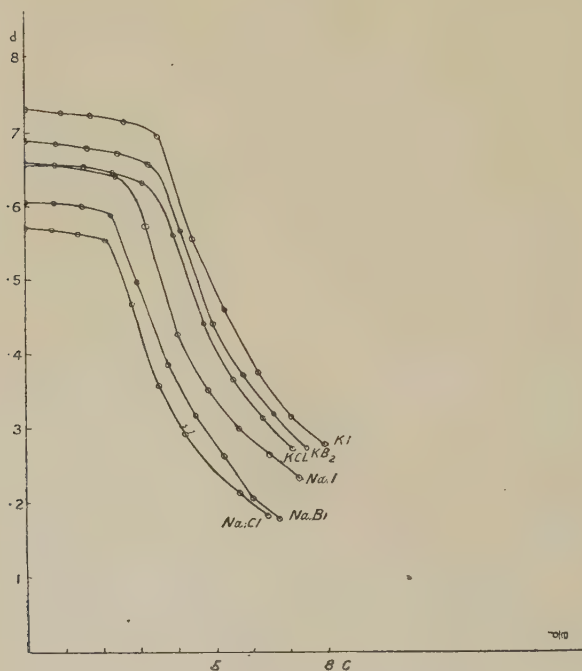
Fig. 4 shows also the graphs of (c, d) obtained in a similar way for NaBr, NaI, KCl, KBr, KI.

If we now take an arbitrary value of c for Na, say 3, we obtain from the curves for NaCl, NaBr, NaI the values .445, .495, .608 of d for Cl, Br, and I respectively. From the curves for KCl, KBr, KI, the values of c for K which correspond to these values of d are seen to be 4.7, 4.56, 4.1. In this way the table given below is drawn up. If the value

c for Na.	d for Cl.	d for Br.	d for I.	c for K given by		
				KCl.	KBr.	KI.
0 Å	.57 Å	.605 Å	.658 Å	3.9 Å	3.8 Å	3.9 Å
1	.567	.603	.657	3.9	3.8	3.9
2	.556	.590	.645	3.95	3.9	4.0
2.5	.510	.570	.640	4.3	4.1	4.0
3	.445	.495	.608	4.7	4.56	4.1
4	.315	.363	.430	6.2	5.9	5.75
5	.236	.277	.334	—	7.2	6.7

assumed for c for Na is the correct one, it is clear that the three values of c for K obtained in this way will be the same.

Fig. 4.

Graph showing relation between c and d .

Hence it is seen that the solution must be in the region

$c=0$ to 2.5 \AA for Na,

$c=3.8 \text{ \AA}$ to 4.0 \AA for K,

$d=.570 \text{ \AA}$ to $.510 \text{ \AA}$ for Cl,

$d=.605 \text{ \AA}$ to $.57 \text{ \AA}$ for Br,

$d=.66 \text{ \AA}$ to $.64 \text{ \AA}$ for I.

A method of trial and error readily gives the following values as those of best fit:—

c for Na = 2.2 \AA ,

c for K = 3.95 \AA ,

d for Cl = $.555 \text{ \AA}$,

d for Br = $.590 \text{ \AA}$,

d for I = $.645 \text{ \AA}$.

Finally, the compressibility is calculated thus :—

For NaCl, when d and c are $\cdot 555 \text{ \AA}$ and $2\cdot 2 \text{ \AA}$, d/a and c/a are $\cdot 1970$ and $\cdot 7631$ respectively. Hence, from fig. 3, $x = \cdot 231$, and therefore, from fig. 2, $A = 12\cdot 4$. This gives a value $4\cdot 139 \times 10^{-12}$ for the specific compressibility. This process was carried out for all the salts under consideration, and the following values for the compressibility were obtained :—

	Compressibility (calculated).	Compressibility (observed).
NaCl	$4\cdot 139 \times 10^{-12}$	$4\cdot 11 \times 10^{-12}$
NaBr	5\cdot 099 "	5\cdot 08 "
NaI	6\cdot 990 "	6\cdot 9 "
KCl	5\cdot 061 "	5\cdot 03 "
KBr	6\cdot 351 "	6\cdot 23 "
KI	8\cdot 660 "	8\cdot 6 "

The observed values of the compressibility are taken from the paper quoted above (T. W. Richards and G. Jones, Journ. Am. Chem. Soc. xxxi. p. 176).

The atomic diameters of Cl, Br, and I, as given by Prof. W. L. Bragg (Phil. Mag. August 1920, p. 180), are $2\cdot 10$, $2\cdot 38$, $2\cdot 80 \times 10^{-8} \text{ cm}$.

$$\text{Since } \frac{\cdot 590 - \cdot 555}{\cdot 645 - \cdot 555} = \cdot 39, \text{ and } \frac{2\cdot 38 - 2\cdot 10}{2\cdot 80 - 2\cdot 10} = \cdot 4,$$

the values of d when plotted against the atomic diameters will fall very nearly on a straight line.

As is shown below, the diameter of the cube of electrons surrounding an atom is of the order of the atomic diameter.

	NaCl.	NaBr.	NaI.	KCl.	KBr.	KI.
Diagonal of cube ...	1\cdot 9784	2\cdot 132	2\cdot 354	1\cdot 8904	2\cdot 022	2\cdot 220
Atomic diameter ...	2\cdot 10	2\cdot 38	2\cdot 80	2\cdot 10	2\cdot 38	2\cdot 80
Ratio	\cdot 942	\cdot 896	\cdot 841	\cdot 900	\cdot 858	\cdot 793

Using the values of c to determine the wave-length for the specific photo-electric effect by the method given by Sir J. J. Thomson (Phil. Mag. April 1922, p. 732), we get the following results :—

	λ (calculated).	λ (observed).
Na	3784	3400
K	4216	4400

The above results were applied to the silver salts.

Silver chloride and silver bromide crystallize in a simple cube of edge 2.78 \AA and 2.89 \AA respectively, the arrangement of the atoms being the same as in NaCl (Wilsey, Phil. Mag. vol. xlii. p. 262, 1921).

If we suppose that the silver contributes one electron to the chlorine or bromine octet, then, using the values of d just obtained ($.555 \text{ \AA}$ for Cl and $.590 \text{ \AA}$ for Br), a calculation similar to that undertaken for NaCl shows that the following values of c for silver give results in agreement with the observed value of the compressibility:—

$$\begin{aligned} \text{For } \text{AgCl}, c &= 4.575 \text{ \AA}; \\ \text{AgBr}, c &= 4.590 \text{ \AA}. \end{aligned}$$

Taking as the mean of these values, c for silver $= 4.580 \text{ \AA}$, the following are the values calculated for the compressibility:—

	Compressibility (calculated).	Compressibility (observed). (T. W. Richards & G. Jones, <i>loc. cit.</i>)
AgCl	2.30×10^{-12}	2.22×10^{-12}
AgBr	2.68 „	2.59 „

Specific Inductance Capacity of Salts.

A calculation of the specific inductive capacity of sodium chloride and of potassium chloride was made thus:—

In an electric field X the atoms and electrons in the crystal undergo the following displacements:—

- (i.) The framework of the alkali atoms is displaced relatively to that of the chlorine atoms.
- (ii.) The shells of electrons surrounding the chlorine atoms are displaced relatively to these atoms.
- (iii.) The shells of electrons surrounding the alkali atoms are displaced relatively to these atoms.

Let us consider these effects separately, when the electric field is parallel to the edge of the cube.

(i.) To calculate this effect, regard the atoms as charges $+e$ and $-e$. Suppose the displacement of the lattice of the alkali atoms relative to that of the chlorine atoms is δz .

Then, from the equilibrium of a displaced atom, we have

$$Xe = \frac{14}{3} \cdot \frac{\alpha}{a^4} \cdot e^2 \cdot \delta z,$$

when the attraction between unlike atoms is $\left(\frac{1}{r^2} - \frac{\alpha}{r^3}\right)e^2$ and the effect of the 26 nearest atoms is considered.

To find α , consider the potential energy V of the atom in the absence of the electric field. It is found that

$$V = -e^2 \left(\frac{1.4558}{a} - \frac{3.333}{2a^2} \alpha \right),$$

when a repulsion $\frac{e^2}{r^2}$ is assumed between atoms of the same kind.

For equilibrium, $\frac{\partial V}{\partial a} = 0$; hence $\frac{\alpha}{a} = .4367$.

Now, in unit volume there are $1/2a^3$ atoms of each kind.

Hence the electric moment per unit volume

$$\begin{aligned} &= \delta z \cdot e \cdot /2a^3 \\ &= \frac{3}{28} \cdot \frac{X}{.4367}. \end{aligned}$$

This is equal to $\frac{K-1}{4\pi} \cdot X$.

Therefore $\frac{K-1}{4\pi} = .2453$.

(ii.) If we consider the equilibrium of an electron of the outermost shell surrounding the chlorine atom in the displaced condition, we find that the restoring forces exerted by the other atoms on the electron are small compared with the force exerted by the chlorine atom itself, and that the latter is

$$\frac{7e^2 \cdot d \cdot \delta z}{27y^4},$$

where δz is the displacement of the electron relative to the chlorine atom measured in the direction of the field, and d , y are the quantities defined in the earlier part of this paper.

The electric moment per unit volume is therefore

$$\frac{8 \cdot e \cdot \delta z}{2a^3} = \frac{4.27}{7} \cdot \frac{y^4}{da^3} \cdot X.$$

On substituting for y , d , and a , we find

$$\frac{K-1}{4\pi} \text{ for NaCl} = \cdot 133,$$

$$\text{for KCl} = \cdot 080.$$

For the inner shells, y^4 decreases rapidly, and the effect of these shells will be neglected.

(iii.) On performing a calculation similar to the above for the outermost shell of the electron still surrounding the alkali atom, we get

$$\frac{K-1}{4\pi} \text{ for NaCl} = \cdot 0031,$$

$$\text{for KCl} = \cdot 013.$$

The value of the specific inductive capacity, when the types of displacement considered above are taken into account, is:—

For sodium chloride,

$$K = 1 + 4\pi[\cdot 2453 + \cdot 133 + \cdot 0031]$$

$$= 5\cdot 793;$$

and for potassium chloride,

$$K = 1 + 4\pi[\cdot 2453 + \cdot 080 + \cdot 013]$$

$$= 5\cdot 252.$$

The observed values of K are :—

Observed	Starke.	W. Schmidt.	Rubens & Nicols.
NaCl	6·29	5·60	5·18
KCl	4·94	4·75	4·55

The calculated value for NaCl is seen to lie between the extreme observed values, while fair agreement is obtained for KCl.

The values of K (given below) are calculated in the same way. No experimental values are available for comparison in these cases :—

NaBr	$K = 5\cdot 914$
NaI	6·031
KBr	5·289
KI	5·363

Summary.

This paper contains a calculation of the compressibility of certain cubic crystals—namely, the chlorides, bromides, and iodides of sodium and potassium, and the chloride and bromide of silver, and also of the specific inductive capacity of sodium chloride and of potassium chloride. A comparison of the calculated with observed values shows that satisfactory agreement is obtained.

This investigation was suggested by Prof. Sir J. J. Thomson, to whose advice and help its completion is also due. I have pleasure in taking the same opportunity of expressing my thanks to the Department of Scientific and Industrial Research for a grant which enabled the work to be undertaken.

XCI. *The Variation of the Photo-electric Activity of a Potassium ferro-cyanide solution with the Concentration of the solution.* By J. H. J. POOLE, *Sc.D.**

IN the course of some previous experiments on the photo-electric theory of vision, it was observed that an aqueous solution of potassium ferro-cyanide exhibited a pronounced photo-electric effect when illuminated by the light of a carbon arc. It was felt at the time that possibly, by measuring the variation of activity of the solution with concentration, some information as to the origin of the photo-electron in the solution might be obtained. Thus, if we consider any dissolved salt, it is plain that there are three possible sources of the photo-electron, *i. e.*, the positive ion, the negative ion, or the undissociated molecule. It is evident that the shape of the curve connecting the activity of the solution with the concentration will depend on which of these three possible origins is the real one, as the degree of the dissociation of the solute will depend on the concentration. Thus in a general way we should expect that if either the positive or the negative ion were responsible, then the rate of increase of activity with concentration would diminish as the concentration increased, while the reverse would hold if the undissociated molecule only emitted the photo-electron. If, however, one radicle of the salt is photo-electric, whether in the combined or ionized condition, the law connecting the activity with the concentration should be a simple linear one.

* Communicated by Prof. J. Joly, F.R.S.

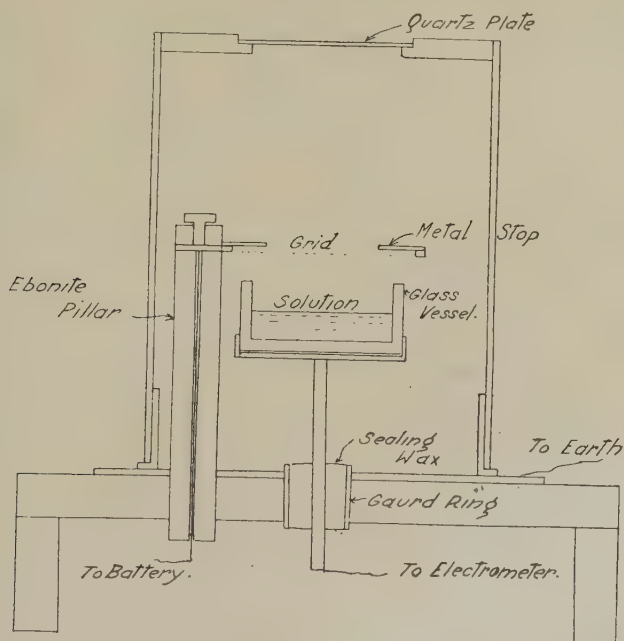
The first attempts at measuring the photo-electric activity of various concentrations were made with a continuous current carbon arc. It was found, however, that consistent results could not be obtained owing to variations in the quantity of ultra-violet light emitted by the arc. Every attempt was made to keep the arc steady by carefully regulating the current through it, but in the end the carbon arc had to be abandoned. It was then decided to use a mercury arc in quartz as a source of light, and after some delay a suitable form of mercury arc was obtained. This arc emitted an approximately constant quantity of ultra-violet light when it had been running for about three-quarters of an hour or more. An ammeter was placed in series with it, so that the current through the arc could be kept constant by means of a regulating resistance.

A Dolezalek quadrant electrometer in conjunction with a special form of ionization vessel was used to measure the electronic current from the solution. The sensitivity of the electrometer could be quickly ascertained by an arrangement by which a known small voltage could be applied to one quadrant. The capacity of the electrometer and ionization vessel was known from previous determinations, and thus the current corresponding to any rate of increase of voltage of the quadrant could be quickly calculated. A sketch of the ionization chamber is shown. The solution to be tested is contained in the glass vessel which fits on top of the central metal platform. The under side of the glass vessel is covered with tinfoil and electrical connexion between this foil and the solution is made by a piece of platinum ribbon which passes over the upper edge of the vessel and dips into the solution. In practice it was found necessary to keep the ribbon slightly greasy where it passed over the edge of the vessel, as otherwise the solution tended to creep out along the ribbon. The metal table on which the glass vessel rests is supported on a central brass pillar which passes through an insulating bushing of sealing-wax in the floor of the ionization chamber. The lower end of this pillar is connected to the isolated quadrant of the electrometer, so that the solution in the glass vessel is directly connected to this quadrant. The advantages of this design are two-fold; firstly, the solution to be tested only comes in contact with glass and platinum and hence we eliminate any effects which might be caused by chemical action between the solution and the containing vessel; and secondly, we can very quickly remove the vessel from the ionization chamber when we desire to substitute a different solution. This point is of

some importance as, owing to possible variations in the intensity of the source of light, it is desirable to be able to test the various solutions as quickly after one another as possible.

To facilitate the escape of the electron from the solution an accelerating electric field was applied in the usual manner to the copper gauze grid fitted, as shown in sketch, over the surface of the solution. This grid was connected to the positive terminal of a high tension battery of about 300 volts

Fig. 1.



pressure. It was found that this voltage was capable of producing approximate saturation in the electronic current even with the strongest solutions. To ensure, however, that no variation in the distance between the surface of the solution and the grid should affect the value of the current, a standard quantity of the solution was always used. Probably at pressures above 300 volts this precaution is not very essential, but at lower pressures the current depended to quite a large extent on the quantity of solution in the glass vessel. This effect was attributed to the fact that the

magnitude of the accelerating field will diminish as the quantity of solution is decreased owing to the increased distance between the grid and the solution, and hence unless the field is sufficient to produce the saturation current in any case, the current will fall off with the decrease in quantity of the solution.

It is very necessary in experiments of this nature that it should be quite plain that the photo-electron is really emitted by the solution and not by the solid containing vessel. For this reason the grid was fitted with a stop, which only allowed the light to fall on the central portion of the liquid surface and not on the walls of the vessel. This arrangement will largely reduce the possibility of electrons being emitted by the containing vessel, but there may be still a few emitted owing to scattered light. However, the results show that the effect, if any, must be small, as the activity of pure water when measured in this apparatus is quite small. It is probable that the amount of scattered light would be independent to a large extent of the solution in the vessel, and hence for the stronger solutions the maximum error due to this cause could not exceed the apparent activity of the pure water and would in consequence be a small one. Owing to the fact that it is the rise in voltage of the isolated central vessel that is measured, no error will be caused by a possible emission of electrons by the metallic sides of the ionization vessel, as all such electrons will be attracted to the grid by the electric field. For the same reason no photo-electrons emitted by the grid itself will leak back to the solution.

The top of the ionization chamber is cylindrical and fits over a brass flange fixed to the floor of the chamber, so that it can be quickly removed. The exciting light is admitted through a quartz window in this top. In the earlier experiments a speculum metal mirror was used to direct the light of the mercury arc on to this window, but this mirror was abandoned later on, and the mercury arc arranged to shine directly downwards on the solution. This procedure is not without its objections, but it was found preferable to using the mirror which not only was not a very efficient reflector of ultra-violet light, but also seemed to vary in efficiency owing to possible changes in its polish. To eliminate as far as possible any error due to changes in the relative positions of the ionization vessel and the mercury arc both pieces of apparatus were clamped firmly to the bench, and these clamps never interfered with during the course of the experiments. It was not necessary to tilt

the mercury vapour lamp in order to strike the arc and hence no vibration was caused in starting the lamp. No quartz lenses were used to concentrate the light of the arc on the solution, as the only one of suitable size available seemed rather to decrease than to increase the effect. This was probably due to the lens being too thick and absorbing a large amount of the active shorter wave-lengths in the light beam.

The solutions of potassium ferro-cyanide used were prepared from the pure salt, supplied by Kahlbaum, and distilled water. The water was stored in glass and hence contained a small amount of dissolved impurities. All solid matter was removed from the solution by careful filtration, as the presence of any dust particles in the solution increases its activity very considerably. Thus if a solution is left exposed to the atmosphere for a few hours, and its activity then measured without disturbing the surface, it will be found to be considerably greater than the normal owing to the layer of dust deposited on the solution, and this effect can be removed nearly entirely by stirring up the liquid so as to distribute the dust through it. On this account the solutions after filtration should be exposed to the atmosphere as little as possible, and the solution transferred from its flask to the ionization chamber as quickly as can be arranged. In practice the solution had first to be transferred to a burette so that a known volume might be run into the testing vessel, but the delay caused by this operation is slight, and as it is the lower part of the liquid in the burette which is used, no dust falling on its upper surface is likely to enter the vessel.

The method of conducting an experiment was as follows. The mercury arc was first turned on to allow it to come to a steady state. While the arc was heating up, the electrometer needle was charged, and the sensitivity of the instrument measured. The solution to be tested was then placed in the ionization vessel, and the grid connected to the high tension battery. By this time the arc was probably moderately steady, and the time taken for the electrometer spot of light to move through a known number of scale divisions, when the quadrant was isolated, was noted. A shutter was fitted in the path of the incident beam of ultra-violet light by which the light could be cut off at will. Several readings of the rate of leak were taken, and then the solution was removed from the chamber, a fresh solution inserted and the process repeated.

The chief trouble in these experiments arose from the fact

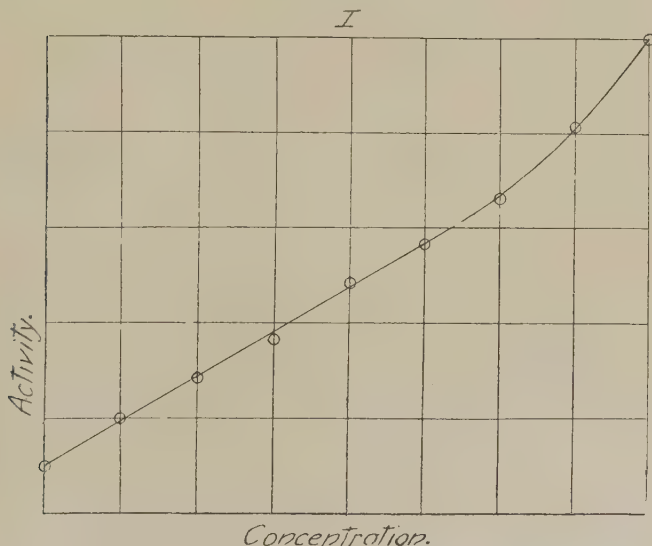
that the mercury lamp was always apparently liable to vary in an erratic manner. As far as the visual light from it was concerned, the arc burnt very steadily, but the amount of ultra-violet light entering the ionization vessel, as measured by the photo-electric discharge from the solution, was not constant. This effect was not due to photo-electric fatigue of the solution, as the activity was as prone to increase with time as to diminish. To eliminate errors due to this cause, the plan adopted was to measure the activity of the strongest solution at frequent intervals during the course of an experiment, and if its value was found to vary by more than about 4 per cent., the readings obtained for the other solutions were neglected.

The table given shows the results of the five most satisfactory series of experiments performed. The number of a solution is simply proportional to its concentration. Solution No. 8 was the strongest solution used and contained 28 grm. of $K_4Fe(CN)_6$ to 100 c.c. of pure water. The other solutions were made up from this solution by dilution with distilled water. As it was found that the activity of the No. 8 solution varied slightly from day to day, owing possibly either to actual variations in the mercury arc itself or to differences in the absorptive power of the air and the quartz window due to differing hygrometric conditions, the activity of this solution has been taken as 100 for each experiment and the activities of the other solutions calculated on this basis. It may be stated that the actual average value of the electronic current per sq. cm. of the strongest solution comes out to be about 8×10^{-14} ampere, or about 5×10^3 electrons per sec. If we assume that a layer only 10^{-8} cm. thick of the solution is affected, this shows that only about one molecule in 10^7 of the potassium ferro-cyanide present in this layer emits an electron every second.

Solution Number.	Activity.					
	I.	II.	III.	IV.	V.	Mean.
8	100	100	100	100	100	100
7	80	82	85	80	78	81
6	62	69	65	72	61	66
5	59	59	51	57	57	57
4	51	48	42	45	53	48
3	37	33	39	34	39	36
2	29	31	29	26	24	28
1	18	19	25	17	19	20
0	4	7	18	11	8	10

The mean value of the activity for each solution has been plotted against the concentration in the following curve. The irregularities in the values of the activity for the various concentrations are probably due to fluctuations in the character of the light, which might not affect a strong and a weak solution in the same way. It is hoped, however, that by taking mean values this error may be eliminated, and the fit of the points on the curve is such as to encourage this view. If we plot the values for any single series of values a curve of similar shape to the main curve is obtained, but usually the observed points do not lie so well on the curve.

Fig. 2.



The curve shows that at the lower concentrations the activity is a simple linear function of the concentration, but that for the stronger solutions the activity increases more rapidly than the concentration. This fact would appear to favour the view that the undissociated molecule is responsible for the photo-electric properties of the solution, but before entering further into this point it may be well to consider briefly whether the range of the photo-electron in the solution itself could have any importance.

Let r = range of electron in solution.

If molecule is in the surface, let the number of electrons

emitted by molecule per second $= kI$, where I is the intensity of incident illumination. When molecule is at a distance x below the surface, only a fraction of the electrons emitted by the molecule will escape.

To determine this fraction, describe a hemisphere of radius r about the molecule. The ratio of the number of electrons

Fig.3.



escaping from the surface to the number emitted by the molecule may be taken as equal to the ratio of the area of the spherical cap cut off by the surface to the area of the hemisphere. The area of this cap is equal to $2\pi r(r-x)$,

hence the value of the fraction escaping will be $\frac{r-x}{r}$.

Let us now consider a layer of area a and thickness dx at a depth x below the surface. Let the number of electrons which escape per second from the liquid and have their origin in this layer be dn . Then we have

$$dn = kI Na \left(1 - \frac{x}{r}\right) dx,$$

where N = number of molecules of solute per c.c.

and I = intensity of illumination in the layer.

Hence n , the total number of electrons escaping from an area a of the liquid per second, is given by the equation

$$n = \int_0^r kI Na \left(1 - \frac{x}{r}\right) dx.$$

There are two main cases which may be considered in the solution of this equation. In the first case we may consider that owing to the very small depth of the layer the intensity of illumination will be constant throughout the layer, or secondly, we may assume that this is not true, but that I is a function of the depth and concentration.

Case I.—Let intensity of incident light-beam be I_0 . Then in our expression for n we may write $I = I_0$.

Hence

$$\begin{aligned} n &= kI_0 Na \int_0^r \left(1 - \frac{x}{r}\right) dx. \\ &= kI_0 Na \frac{r}{2}. \end{aligned}$$

This shows that if r , the range of the electron, is independent of the concentration, then the activity of a solution should be simply proportional to the concentration, if the intensity of the light-beam is constant. For the weaker solutions of potassium ferro-cyanide this law seems to be fairly accurately obeyed, but it does not hold for the stronger solutions.

Case II.—If we do not consider the illumination throughout the layer to be constant, the simplest assumption to make is that it will fall off with depth according to an exponential law. Let us accordingly assume that $I = I_0 e^{-\lambda x}$. The value of λ will obviously depend on the concentration, and may be written in the form $\lambda = aN + b$ where a and b are constants, the b term representing the absorption of the solvent. Our expression for n will now become

$$\begin{aligned} n &= k I_0 N a \int_0^r e^{-\lambda x} \left(1 - \frac{x}{r}\right) dx \\ &= k I_0 N a \int_0^r e^{-\lambda x} \left(\frac{x}{\lambda r} + \frac{1}{\lambda^2 r} - \frac{1}{\lambda}\right) \\ &= k I_0 N a \left[\frac{1}{\lambda} - \frac{1}{\lambda^2 r} (1 - e^{-\lambda r}) \right] \\ &= k I_0 N a \left[\frac{r}{2} - \frac{\lambda r^2}{3} + \frac{\lambda^2 r^3}{4} - \text{etc.} \right]. \end{aligned}$$

If $\lambda = 0$, that is if we neglect the effect due to absorption, this formula reduces to the one obtained in the previous case. Now λr will always be small, so that we may neglect higher powers of λr than the first. Thus,

$$n = k I_0 N a r \left(\frac{1}{2} - \frac{\lambda r}{3} \right).$$

But

$$\lambda = aN + b.$$

Therefore

$$n = k I_0 N a r \left(\frac{1}{2} - \frac{br}{3} - \frac{aNr}{3} \right).$$

If we consider, as before, that r is independent of N , we may write this equation in the form

$$n = eN(f - gN),$$

where e , f , and g are independent of N .

Differentiating this expression with regard to N , we get

$$\frac{dn}{dN} = e(f - 2gN).$$

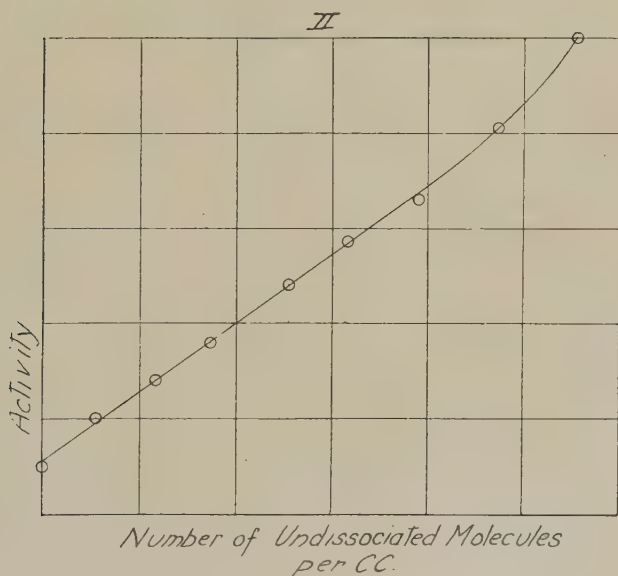
As this shows that the value of $\frac{dn}{dN}$ decreases as we increase the concentration, it entirely fails to explain the experimental results obtained, and accordingly we must look elsewhere for a feasible explanation.

As has already been mentioned, there are three possible sources of the photo-electron in the solution, namely, the positive ion, the negative ion, and the undissociated molecule. The evidence seems, however, to render it very unlikely that the positive ion could be responsible for the photo-electron, as it will already have lost one electron, and is therefore extremely unlikely to lose a second. This view is further confirmed by the fact that potassium ferri-cyanide was found to be nearly entirely inactive in solution, showing that the photo-electric properties must be due to the negative radicle. Previous investigators have also found that the activity of the salts of potassium depends on the negative radicle; thus while potassium chloride decreases the activity of pure water, potassium sulphate increases it considerably. It now remains to be decided whether the negative radicle is active only when not ionized, or whether its state of ionization is immaterial. The possibility that it is only the ionized form that is active may be dismissed, as if this were the case, the slope of the activity curve should decrease with concentration, not increase as the experimental results show it does. The lower linear portion of the curve certainly favours the view that both the negative ion and the undissociated molecule are equally active, but the rapid increase of activity for the stronger solutions is not very easily explained on this hypothesis.

To further investigate this point, the electrical conductivities of the various solutions were measured with a Kohlrausch cell and bridge, and the percentage of undissociated molecules present in each solution calculated from the value of the conductivity for very dilute solutions, on the usual assumption that the change of equivalent conductivity of a solution with concentration is entirely due to the variation in the degree of dissociation of the solute. Curve II. (fig. 4) has been plotted from these results. The abscissæ are proportional to the number of undissociated molecules per c.c. and the ordinates to the activity of the solution. If the activity were due to the undissociated molecules only, and if the chance of a molecule emitting an electron were unaffected by the presence of other molecules of the solute, this curve

would be a straight line. This is not the case, however, as the curve bends decidedly upwards for the higher concentrations, showing that the increase in the number of undissociated molecules is not sufficient to explain the increased activity. There are two possible ways out of this difficulty. One is to suppose that the concentration of the molecules in the surface increases more rapidly for the stronger solutions than the general concentration throughout the liquid. If the surface tension of the solution depends on its strength, we might expect some such effect as this to arise, as in this case

Fig. 4.



the concentration of the solute in the surface layer would be different from the concentration throughout the bulk of the liquid. Dorsey (Phil. Mag. 1897) has shown that in general the surface tension of aqueous salt solutions is greater than that of pure water, and this would lead to the surface layer being poorer in the solute than the rest of the liquid. He also showed, however, that the surface tension of the solution was a simple linear function of the concentration, and this would naturally lead us to suppose that the concentration in

the surface layer was proportional to the general concentration in the liquid, although not equal to it. If this view is correct, we cannot explain the increased activity of the strong solutions on these grounds, and we are forced to turn to the second alternative, namely that the activity of a molecule of the solute is not independent of the presence of other similar molecules, but increases as the concentration is increased. This seems to be a plausible explanation as in many cases it has been found that a body in the solid state is much more photo-electric than in the liquid state. Thus in the very strong solutions we might expect that the solute was not entirely broken up into molecules and ions, but that some of the molecules were still associated into larger groups. As these groups would approximate more closely to the conditions of the solid state, it would be natural to suppose that the activity of the group as a whole would be greater than the sum of the activities of its component molecules when isolated, and hence the increased activity of the stronger solutions would be explained.

Summary of Paper.

Experiments on the variation of the photo-electric activity of a potassium ferro-cyanide solution with concentration are described. It is shown that :—

- (a) The negative radicle is probably responsible for the photo-electric properties of the solution.
- (b) The relative increase of activity of the stronger solutions cannot be accounted for either by the possible effects of the range of the photo-electron in the solution, or by the increase in the number of undissociated molecules per c.c. of solution. It seems probable that this increase is to be attributed to the effect of a possible association of the molecules of the solute in the more concentrated solutions.

Physical Laboratory,
Trinity College, Dublin.
February, 1923.

XCII. *On the Velocity of Sound in Liquids contained in Circular Cylinders with slightly Elastic Walls.* By H. G. GREEN, M.A.*

History and aim of the Paper.

EXPERIMENTING in 1847, Wertheim found that the velocity of sound in an organ-pipe completely immersed in water was reduced to 1173 metres per second, and he put forward the theory that the water in the pipe behaved as a quasi-elastic solid. Helmholtz (1848) by a general discussion showed that this theory could not be correct, and suggested that the effect was due to yielding of the pipe-walls, an interpretation supported by Kundt and Lehmann (1874) and by Dvořák in their experiments with water by the method of Kundt's dust tube. We propose to obtain an approximate expression for the velocity on the hypothesis that the change is entirely due to the give of the walls, and to compare results so obtained with those of experiment. This comparison unfortunately can only be rough, from the absence of full data of the pipes employed.

References.

An account of the experiments to be discussed may be found in Barton's 'Sound,' 4th edition. In the treatment of the hollow cylinder, the methods used by Chree (Cambridge Phil. Soc. Trans. vol. xiv. 1889) and Love for the vibrations of solid ones will be followed. Paragraphed references under the latter name are to his 'Mathematical Theory of Elasticity,' 3rd edition. References "G. and M." are to the 'Treatise on Bessel Functions' (Gray and Mathews, 1895), while necessary physical constants are from Landolt-Börnstein's Tables.

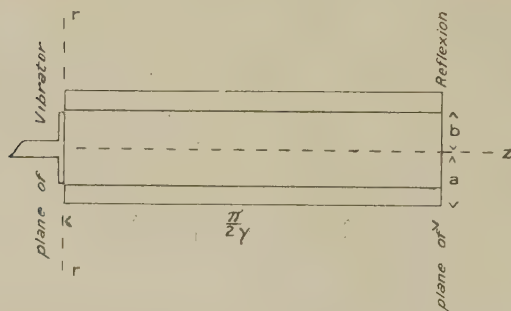
Notation.

The general notation of Love will be adopted, using cylindrical coordinates. The pipe (fig. 1) is to have its axis along the axis of z , and, in the equilibrium state, to have external and internal radii a , b respectively. The length of the sound-wave $\left(\frac{2\pi}{\gamma}\right)$ is supposed to be large compared with a and b , but the discussion is not confined .

* Communicated by Prof. E. H. Barton, F.R.S.

to the case of the "thin-walled" pipe. The plane of reflexion, supposed fixed in space by external agency, is taken as the plane $z = \frac{\pi}{2\gamma}$.

Fig. 1.



We shall first consider the displacements of the material of the pipe under a radial pressure $P \cos nt \sin \gamma z$ on the inner surface with trial displacements

$$u_r = U \cos nt \sin \gamma z, \quad u_\theta = 0, \quad u_z = W \cos nt \cos \gamma z,$$

where U and W are functions of r . [cf. Love, § 199.]

The equations of motion, as in Love (§§ 199 to 201), reduce to

$$\frac{\partial^2 \Delta}{\partial r^2} + \frac{1}{r} \frac{\partial \Delta}{\partial r} + h^2 \Delta = 0, \quad \dots \quad (1)$$

$$\frac{\partial^2 \varpi_\theta}{\partial r^2} + \frac{1}{r} \frac{\partial \varpi_\theta}{\partial r} - \frac{\varpi_\theta}{r^2} + k^2 \varpi_\theta = 0, \quad \dots \quad (2)$$

where

$$h^2 = n^2 \rho / (\lambda + 2\mu) - \gamma^2, \quad k^2 = n^2 \rho / \mu - \gamma^2,$$

$$\Delta = \frac{1}{r} \frac{\partial (r u_r)}{\partial r} + \frac{\partial u_z}{\partial z},$$

and

$$2\varpi_\theta = \frac{\partial u_r}{\partial z} - \frac{\partial u_z}{\partial r};$$

or

$$\Delta = \left(\frac{\partial U}{\partial r} + \frac{U}{r} - \gamma W \right) \cos nt \sin \gamma z, \quad \dots \quad (3)$$

$$2\varpi_\theta = \left(\gamma U - \frac{\partial W}{\partial r} \right) \cos nt \cos \gamma z. \quad \dots \quad (4)$$

The solutions of equation (1) for Δ are of types $J_0(hr)$, $Y_0(hr)$, and of equation (2) for ϖ_θ of types $J_1(kr)$, $Y_1(kr)$,

and we have to take U and W of the forms

$$U = \frac{\partial}{\partial r} \{A J_0(hr) + B Y_0(hr)\} + \gamma \{C J_1(kr) + D Y_1(kr)\},$$

$$W = \gamma \{A J_0(hr) + B Y_0(hr)\} + \frac{1}{r} \frac{\partial}{\partial r} \{C r J_1(kr) + D r Y_1(kr)\}.$$

Using the relations between first derivatives of Bessel functions

$$\frac{\partial}{\partial x} J_0(x) = -J_1(x),$$

$$\frac{\partial}{\partial x} J_1(x) = J_0(x) - \frac{1}{x} J_1(x),$$

or

$$\frac{\partial}{\partial x} x J_1(x) = x J_0(x), \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

with similar expressions in the Y 's, [G. and M. pp. 13, 14] these may be re-written

$$U = -h \{A J_1(hr) + B Y_1(hr)\} + \gamma \{C J_1(kr) + D Y_1(kr)\}, \quad (6)$$

$$W = \gamma \{A J_0(hr) + B Y_0(hr)\} + k \{C J_0(kr) + D Y_0(kr)\}, \quad (7)$$

and hence

$$\Delta = -(h^2 + \gamma^2) (A J_0(hr) + B Y_0(hr)) \cos nt \sin \gamma z. \quad . \quad . \quad (8)$$

The radial tractive force is given by

$$\widehat{rr} = \lambda \Delta + 2\mu \frac{\partial u_r}{\partial r},$$

and the tractive force parallel to the axis by

$$\widehat{rz} = \mu \left(\frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r} \right);$$

and so by substitution from (6), (7), and (8) we obtain after simplification by (5)

$$\widehat{rr} / \cos nt \sin \gamma z$$

$$\begin{aligned} &= A \left[(-\lambda(h^2 + \gamma^2) - 2\mu h^2) J_0(hr) + \frac{2\mu h}{r} J_1(hr) \right] \\ &+ B \left[(-\lambda(h^2 + \gamma^2) - 2\mu h^2) Y_0(hr) + \frac{2\mu h}{r} Y_1(hr) \right] \\ &+ 2\mu \gamma C \left[k J_0(kr) - \frac{1}{r} J_1(kr) \right] \\ &+ 2\mu \gamma D \left[k Y_0(kr) - \frac{1}{r} Y_1(kr) \right], \quad . \quad . \quad . \quad . \quad (9) \end{aligned}$$

and

$$\begin{aligned} \widehat{rz} / \cos nt \cos \gamma z &= -2\mu \gamma h [A J_1(hr) + B Y_1(hr)] \\ &- \mu (k^2 - \gamma^2) [C J_1(kr) + D Y_1(kr)]. \quad (10) \end{aligned}$$

Now for a modulus x ,

$$J_0 = 1 - \frac{x^2}{4} + \dots,$$

$$J_1 = \frac{x}{2} - \frac{x^3}{16} + \dots,$$

$$Y_0 = J_0 \log x + 4 \left(\frac{J_2}{2} - \frac{J_4}{4} + \dots \right),$$

$$Y_1 = J_1 \log x - \frac{1}{x} - \frac{J_1}{2} + \frac{6 \cdot 3}{2 \cdot 4} J_3 - \dots;$$

[G. and M. p. 22]

and where x is small we can write in (9), (10) to obtain a first approximation, 1 , $\log x$, $\frac{x}{2}$, $-\frac{1}{x}$ for $J_0(x)$, $Y_0(x)$, $J_1(x)$, $Y_1(x)$ respectively (that is, the leading terms in the expansions of the functions), and retaining only the largest terms in the multipliers of A, B, C, and D, we have

$$\begin{aligned} \widehat{r}r / \cos nt \sin \gamma z \\ = -A[\lambda(h^2 + \gamma^2) + \mu h^2] - B \frac{2\mu}{r^2} + C\mu\gamma k + D \frac{2\mu\gamma}{kr^2}, \end{aligned}$$

$$\begin{aligned} \widehat{r}z / \mu \cos nt \cos \gamma z \\ = -A\gamma h^2 r + B \frac{2\gamma}{r} - C \frac{(k^2 - \gamma^2)kr}{2} + D \frac{(k^2 - \gamma^2)}{kr}. \end{aligned}$$

We have as boundary conditions:—

$$\text{When } r=b, \quad \widehat{r}r = -P \cos nt \sin \gamma z, \quad \widehat{r}z = 0;$$

$$,, \quad r=a, \quad \widehat{r}r = 0, \quad \widehat{r}z = 0;$$

which give four equations to determine the constants, and lead to, after heavy but straightforward algebra,

$$\frac{A}{\Delta_A} = \frac{-B}{\Delta_B} = \frac{C}{\Delta_C} = \frac{-D}{\Delta_D} = \frac{P}{\Delta_P},$$

where

$$\Delta_A = \mu(k^2 - \gamma^2)(k^2 + \gamma^2) \frac{a^2 - b^2}{a^3 b},$$

$$\Delta_B = (k^2 - \gamma^2) [\lambda(h^2 + \gamma^2)(k^2 - \gamma^2) + \mu h^2(k^2 + \gamma^2)] \frac{a^2 - b^2}{2ab},$$

$$\Delta_C = -\frac{2\mu\gamma h^2}{k} (k^2 + \gamma^2) \frac{a^2 - b^2}{a^3 b},$$

$$\Delta_D = -\gamma k [\lambda(h^2 + \gamma^2)(k^2 - \gamma^2) + \mu h^2(k^2 + \gamma^2)] \frac{a^2 - b^2}{ab},$$

$$\Delta_P = -\mu(k^2 + \gamma^2) [\lambda(h^2 + \gamma^2)(k^2 - \gamma^2) + \mu h^2(k^2 + \gamma^2)] \frac{(a^2 - b^2)^2}{a^3 b^3};$$

also $\lambda(h^2 + \gamma^2)(k^2 - \gamma^2) + \mu h^2(k^2 + \gamma^2)$, which is a factor in three of these expressions, can be re-written as

$$\frac{\lambda n^2 \rho}{\lambda + 2\mu} \left(\frac{n^2 \rho}{\mu} - 2\gamma^2 \right) + \frac{\mu n^2 \rho}{\mu} \left(\frac{n^2 \rho}{\lambda + 2\mu} - \gamma^2 \right),$$

or, after manipulation, as

$$-n^2 \rho \gamma^2 \frac{3\lambda + 2\mu}{\lambda + 2\mu} \left[1 - \frac{v^2}{E/\rho} \right],$$

where $v = n/\gamma$ is the velocity of propagation and $E = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu}$ is Young's modulus.

[It is to be noted that to our degree of approximation the solution breaks down if $v = \sqrt{\frac{E}{\rho}}$. Cf. Chree's result for a solid cylinder.]

From (6) we have

$$U = \frac{r}{2} [-Ah^2 + C\gamma k] + \frac{1}{r} \left[B - \frac{D\gamma}{k} \right],$$

or

$$\frac{U\Delta_P}{P} = \frac{r}{2} [-\Delta_A h^2 + \Delta_C \gamma k] + \frac{1}{r} \left[-\Delta_B + \frac{\Delta_D \gamma}{k} \right];$$

$$\begin{aligned} -\Delta_A h^2 + \Delta_C \gamma k &= -\frac{a^2 - b^2}{a^3 b} (k^2 + \gamma^2)^2 \mu h^2 \\ &= -\frac{a^2 - b^2}{a^3 b} (k^2 + \gamma^2) \mu \cdot \frac{n^2 \rho}{\mu} \left(\frac{n^2 \rho}{\lambda + 2\mu} - \gamma^2 \right) \\ &= \frac{a^2 - b^2}{a^3 b} (k^2 + \gamma^2) \cdot n^2 \rho \gamma^2 \left(1 - \frac{v^2 \rho}{\lambda + 2\mu} \right), \\ -\Delta_B + \frac{\Delta_D \gamma}{k} &= \frac{a^2 - b^2}{2ab} (k^2 + \gamma^2) n^2 \rho \gamma^2 \cdot \frac{3\lambda + 2\mu}{\lambda + 2\mu} \left(1 - \frac{v^2}{E/\rho} \right), \end{aligned}$$

and

$$\frac{U}{P} = \frac{b^2}{2(a^2 - b^2)} \left\{ r \frac{\left(1 - \frac{v^2 \rho}{\lambda + 2\mu} \right) (\lambda + 2\mu)}{\left(1 - \frac{v^2 \rho}{E} \right) (3\lambda + 2\mu)} + \frac{a^2}{r} \right\}.$$

. . . (11)

We are now in a position to discuss the hydrodynamical problem. It is supposed that the waves remain plane and that the pressure variations are small. The displacements of the walls of the pipes are then small, and we can consider

the hydrodynamical pressure on the inner wall as radial instead of normal.

We can take the radial displacement of the inner wall ($r=b$) as $u_r = U \cos nt \sin \gamma z$ under pressure

$$p = P \cos nt \sin \gamma z, \quad . \quad . \quad . \quad (12)$$

where, in accordance with equation (11),

$$\frac{U}{P} = \frac{b}{2(a^2 - b^2)\mu} \left\{ \frac{b^2 \left(1 - \frac{v^2 \rho}{\lambda + 2\mu}\right) (\lambda + 2\mu)}{\left(1 - \frac{v^2 \rho}{E}\right) (3\lambda + 2\mu)} + a^2 \right\}. \quad (13)$$

Let ζ be the liquid displacement at time t relative to z in space. We shall write δ_0 for the density in the unstrained state and δ for that at time t .

To a first approximation the equation of continuity is

$$\delta \left\{ 1 + \frac{2u_r}{b} \right\} \left(1 + \frac{\partial \zeta}{\partial z} \right) = \delta_0, \quad . \quad . \quad . \quad (14)$$

and that of force is

$$-\frac{\partial p}{\partial z} = \delta_0 \frac{\partial^2 \zeta}{\partial t^2}. \quad . \quad . \quad . \quad (15)$$

But by (12),

$$u_r = \frac{U}{P} p,$$

and (14) becomes

$$\delta \left\{ 1 + \frac{2U}{bP} p \right\} \left(1 + \frac{\partial \zeta}{\partial z} \right) = \delta_0,$$

or say

$$\delta(1 + \alpha p) \left(1 + \frac{\partial \zeta}{\partial z} \right) = \delta_0, \\ \text{where } \alpha = \frac{2U}{bP}. \quad . \quad . \quad . \quad (16)$$

But

$$p = K \frac{\delta - \delta_0}{\delta_0} = K \frac{1 - (1 + \alpha p) \left(1 + \frac{\partial \zeta}{\partial z} \right)}{(1 + \alpha p) \left(1 + \frac{\partial \zeta}{\partial z} \right)}, \text{ from (16),} \\ = -K \left(\alpha p + \frac{\partial \zeta}{\partial z} \right) \text{ approx.,}$$

α and $\frac{\partial \zeta}{\partial z}$ being small,

$$\text{or } p(1 + \alpha K) = -K \frac{\partial \zeta}{\partial z}.$$

Hence

$$\frac{K}{1+\alpha K} \frac{\partial^2 \zeta}{\partial z^2} = \delta_0 \cdot \frac{\partial^2 \zeta}{\partial t^2}, \text{ from (15),}$$

or

$$v^2 = \frac{K}{\delta_0} \frac{1}{1+\alpha K}.$$

If we write $v_0 = \sqrt{\frac{K}{\delta_0}}$ as the velocity of plane waves in liquid of unlimited extent, we have therefore

$$v^2 = \frac{v_0^2}{1+\delta_0 \alpha v_0^2}, \quad \dots \dots \dots (17)$$

or

$$v_0^2 = \frac{v^2}{1-\delta_0 \alpha v^2}, \quad \dots \dots \dots (18)$$

where δ_0 is the density of the liquid and

$$\alpha = \frac{1}{(a^2 - b^2)\mu} \left\{ \frac{b^2 \left(1 - \frac{v^2 \rho}{\lambda + 2\mu} \right) (\lambda + 2\mu)}{\left(1 - \frac{v^2 \rho}{E} \right) (3\lambda + 2\mu)} + a^2 \right\}.$$

The quantity $\delta_0 \alpha v^2$ in equation (18) can be given a direct physical meaning. We shall consider the fluxes through the boundaries of a cylinder of radius b and length δz , with its axis along the axis of z and centre at the point z . The velocity q along the axis is then given by

$$q = -\frac{\gamma P}{n \delta_0} \cdot \sin nt \cos \gamma z.$$

The outward flux through the plane faces is given by

$$\pi b^2 \frac{\partial q}{\partial z} \cdot \delta z = \frac{\pi b^2 \gamma^2 P}{n \delta_0} \cdot \sin nt \sin \gamma z \cdot \delta z,$$

and the inward flux through the curved surfaces by

$$-2\pi b \cdot \delta z \cdot \frac{\partial u_r}{\partial t} = 2\pi b n U \sin nt \sin \gamma z \cdot \delta z,$$

and their ratio

$$= \frac{2n^2 \delta_0 U}{\gamma^2 b P} = \delta_0 \alpha v^2.$$

The assumption that the waves are still appreciably plane demands that this ratio should not be large. In the numerical examples which follow, cases where it exceeds

a half have been rejected as beyond the approximations of the formula.

Where Poisson's ratio is near to a quarter and the value of v is considerably less than $\sqrt{\frac{E}{\rho}}$ (less than half of it is sufficient), the ultimate numerical error in taking $\lambda = \mu = \frac{2}{3}E$, and in neglecting the v^2 term in α , is less than that due to errors in the experimental determinations of the elastic constants. In such cases the approximate value of α is $\frac{(a^2 + \frac{2}{3}b^2)}{(a^2 - b^2)}\mu$.

It may be noted that the relations (17), (18) are independent of the frequency employed. If the expression had been carried to the next approximation, terms containing the frequency would have remained (*cf.* Chree's paper), indicating that for a pipe of given length the overtones are not exact harmonics of the fundamental. Experimental results for elastic constants are not usually very reliable beyond two or three significant figures, and further approximation would not add to the numerical accuracy of the formula.

We will now apply the formula to the experimental cases of Kundt and Lehmann (Table I.) and of Dvořák (Table II.) (see Barton, pp. 533, 535). We shall assume an average glass with $\mu = \lambda = 2.4 \times 10^{11}$ dynes per sq. cm., taking v_0 as 1440 m. per sec. and δ_0 as 1. The differences are given as percentages of the experimental result.

[*Note.*—The possible range for μ is 25 per cent. on either side of the one taken. It probably varied from tube to tube.]

TABLE I.

a in mm.	b in mm.	Temp.	v from Experiment.	v from Formula.	% Diff.
16.55	14.35	18.4	1040.4 (2)	1174	+12.9
20	17	17	1227.7 (3)	1198	— 2.4
14.75	11.75	18	1262.2 (3)	1250	— .97
14	10.5	18.5	1357 (2)	1281	— 5.6
13.25	8.25	18.5	1360 (3)	1328	— 2.4
12	7	22.2	1383 (1)	1339	— 3.2

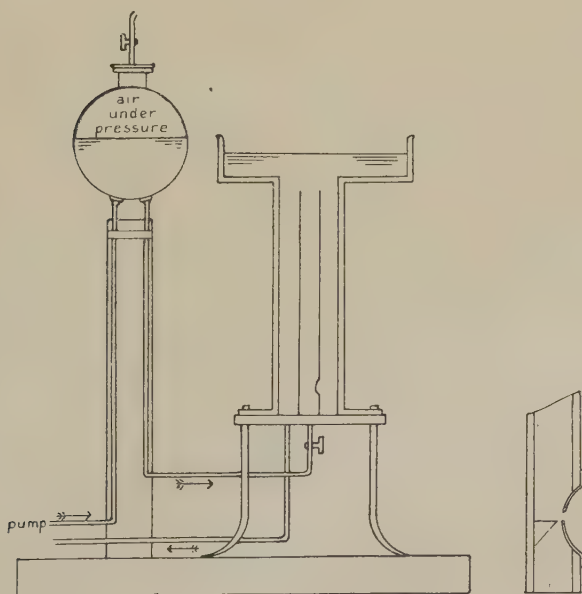
(The experimental results are averages of the numbers of readings indicated in brackets.)

TABLE II.

a in mm.	b in mm.	v from Experiment.	v from Formula.	% Diff.
9.77	8.95	998	1071	+7.3
6.48	5.85	1046	1107	+4.9
4.75	4.23	1164	1133	-2.6
9.5	7.5	1213	1256	+3.5
7.5	5.5	1281	1289	+ .62

Wertheim in 1848 published the results of investigations on the velocities of sound in various liquids, using his organ-pipe method (*Ann. Chim. phys.* (3) xxiii. p. 434, 1848).

Fig. 2.



Finding that for Seine water his result when multiplied by $\sqrt{\frac{3}{2}}$ gave very approximately the result for water unlimited in extent, he devised the quasi-elastic theory, and applied the same correction factor to other liquids. Fig. 2 shows the general arrangement of his apparatus,

TABLE III. A.

TABLE III. B.

Density.	Temp. °C.	v_0 m/s.	$10^6 \times$ compressibility per atmos./cm. ²				v_0 m/s, new theory.
			Calc.	Grassi.		Calc. from new theory.	
Seine water	15	1437	49.1				
Sea-water	20	1453	46.7	43.6		45.0	1479
Solution NaCl	18	1561	34.9	32.1		27.8	1750
Solution Na ₂ SO ₄	20	1525	39.3			34.4	1630
Solution Na ₂ SO ₄	18.8	1583.5	34.8			27.5	1777
Solution Na ₂ CO ₃	22.2	1594	33.7	29.7		26.0	1815
Alcohol (common)	20	1285.9	73.3			85.4	1188
Alcohol (abs.)	23	1159.8	94.7	99.1	116 ¹	117.5	1041
Turpentine	24	1212.3	80.0		84.2 ²	95.4	1109
Ether	0	1159	100.2	111.0	147 ¹	126	1035

¹ From Amagat's results, 1893.² From Quincke's results, 1883.

and Table III.A gives his values for $v_0 (= \sqrt{\frac{3}{2}}v)$. The agreement of the compressibility deduced from these results with those obtained by Grassi by direct methods (1851) gained the support of Tyndall, in spite of Helmholtz's condemnation. Table III.B gives revised values for v_0 and for the compressibility with, in some cases, the values obtained directly by later experimenters. It will be seen that, except in two cases, the new values show better agreement.

In order to obtain this table we have assumed that $\sqrt{\frac{3}{2}}$ is the correct factor for Seine water, and employed it to obtain the pipe constant. Unfortunately, Wertheim used several tubes and took average results without any regular arrangement, so that the deduced values of v_0 are purely tentative. In any case, the sensitiveness of the formula (18) to slight errors in v renders the method unsatisfactory.

In none of these cases is the formula strictly applicable, for the plane of reflexion is not usually fixed in space, nor is the plane of excitement, as far as the tube is concerned, sufficiently free of external restraint. Difficulty also arises from the radial forces over these planes (*cf.* Love, § 201). In working with the dust tube the experimentalist overcomes these difficulties by using a tube of length an odd number of quarter wave-lengths, taking his measurements only in the central section. In Wertheim's apparatus the movement of the plane of vibration is damped by a quantity of "dead" material (no ordinary fastening is rigid from the point of view of these vibrations), but in those cases where he used an open pipe the conditions at the plane of reflexion are closely approached. The neglect of external variations of pressure in the surrounding medium will produce no error in the formula, for the amplitudes of the vibrations set up are small compared with those of the liquid contained in the tube—they would have to be considered in a second approximation.

Summary.

We have obtained a formula for a certain type of forced vibration in a hollow cylinder, and applied it to find the effects of pipe-yield on sound-waves in a liquid in the cylinder.

On application to various experimental results, it is found that the deduced effect shows agreement which is, on the whole, sufficiently close to confirm Helmholtz's theory and

also to neutralize the agreements which led to support of Wertheim's. It cannot, however, be considered sufficiently close to enable calculation to replace experiment wherever considerable accuracy is required, as it might be, for example, in very long pipe-lines for the Transmission of Power by Waves (method of G. Constantinesco).

University College, Nottingham.
February 1923.

XCIII. *The Effect of Current on the Photo-electric Sensitivity of Metals.* By ALLEN G. SHENSTONE, M.A.*

IN the Philosophical Magazine † I have described certain experiments in which the photo-electric sensitivity of a bismuth plate was temporarily increased by the passage of a current through the plate under examination. Further experiments which have been carried out during the past year have not only confirmed the presence and magnitude of that effect, but have shown it to exist in a number of other metals.

There have recently appeared two very important papers on this subject ‡, Hallwachs and Sende and Simon describe experiments in which a strip of platinum was glowed by means of a current for often repeated intervals of 10 seconds. Readings of photo-electric sensitivity were taken between heatings.

It was found that the photo-electric sensitivity increased very rapidly at first to a high value, from which it decreased more gradually to a value which, in some cases, was too small to be detected by the instruments in use. The authors of the papers base their explanation of this phenomenon on the assumption that the changes of photo-electric sensitivity are entirely due to changes in gas-content of the metal surface. The driving off of the adsorbed surface-layer of gas is made responsible for the rise in photo-electric current by allowing the electrons to escape more easily. Further heating then drives out the absorbed gas, this phase corresponding to the gradual fall of current observed. On this explanation their results lead to the conclusion that gas is essential for the photo-electric emission of electrons from

* Communicated by Prof. E. P. Adams, Ph.D.

† Phil. Mag. xli. p. 916 (1921).

‡ Phys. Zeit. xxi. p. 562 (1920); Ann. der Phys. lxxv. p. 697 (1921).

metals. In other words, they do not believe that the photo-electric effect exists at all for pure metals in the range of wave-lengths supplied by a quartz mercury lamp. It is well to point out, however, that their observations were never made on gas-free surfaces, even at the most favourable points in their experiment; for, in a vacuum such as they describe, a metallic surface would be covered by a layer of gas in a very small fraction of a second. This fact renders the authors' explanation of their recuperation curves especially doubtful, since the formation of the surface-layer would prevent the maximum on those curves.

In connexion with those experiments consideration should be given to the work of Millikan * on the effect of temperature on the photo-electric emission from metals. His experiments were carried out in a well-baked-out apparatus, and proved conclusively that between 25° and 125° change of temperature produced no change in the photo-electric emission from copper, gold, nickel, brass, silver, iron, aluminium, magnesium, antimony, zinc, lead. Those experiments covered long periods of time, during which the small changes of temperature used had ample opportunity to produce their maximum effect upon the gas-content of the metals.

The essential difference between the two experiments just described lies in the use by Hallwachs of an electric current through the metal under observation. That the wide divergence of their results and conclusions can be explained by this fact seems probable, from the experiments described by me in *Phil. Mag.* (*loc. cit.*) and from additional work recently carried out. This work indicated distinctly that an electric current can influence the photo-electric sensitivity of a metal directly, independently of its heating effect.

The apparatus used in this new work is essentially the same as that formerly described, except that the electrode has been modified to a conical form to allow a wider beam of light to strike the metal, and to protect the glass walls from charging. A diffusion pump was used during all observations, and always maintained a pressure not measurable on a McLeod gauge. The potential on the plate was varied between -3 and -15 volts, and gave entirely parallel results over that range; for the most part, -15 volts was used. It was thought advisable to eliminate any possible effect of the plate current on the photo-electrons. The light was therefore screened between readings, and the current

* *Phil. Mag.* xiv. p. 188 (1907).

was interrupted during readings. The measurements of photo-electric current were made with a Dolezalek electrometer of sensibility 1000 divisions per volt, earthed through an india-ink resistance of 5×10^8 ohms, giving about 2×10^{-12} ampere per millimetre.

My former observations were all made on plates of cast bismuth; and it was suggested in my paper that a possible explanation of the results obtained was an orientation of the elementary crystals due to the passage of the current. This possibility was satisfactorily disposed of by making observations on plates cut from large crystals of bismuth, obtained by very slow cooling of a melt. Plates cut in various directions gave entirely comparable results. Confirmation of this conclusion was afterwards obtained from the results with films formed by evaporation, which are almost certainly non-crystalline.

The most important point requiring experimental evidence is the question of the effect of temperature. In order first to find what changes of temperature were taking place in the bismuth plate, a constantan-copper thermo-junction was soldered to the back of the plate, the flattened leads being led out through the de Khotinsky cement in the ground-glass seal. With this arrangement it was found that the temperature rise corresponding to a rise of photo-electric current of 16 per cent. was less than 5°C , and corresponding to 30 per cent. was only 24° . From these measurements alone, it seems very improbable that the observed changes of photo-electric current can be ascribed to changes due to temperature.

A few runs were made with a tungsten heating grid inserted behind the bismuth plate. This gave in every case a fall of photo-electric current, which in some cases was very considerable. The results were, however, too irregular to allow them any great weight in the interpretation of the effect.

An apparatus was next constructed to heat the bismuth plate without the use of a current. A brass tube was made to fit the ground seal of the glass apparatus, and the bismuth plate was cemented and wired to the end of this tube. A stream of water of known temperature could then be circulated to bring the plate to that temperature. The arrangement proved to be air-tight up to a temperature of about 50°C ., where the cement began to fail. Over the range from 15° to 50° , the photo-electric current remained unchanged within 2 per cent. Cooling to the neighbourhood of 0°C . lowered the sensitivity by 5 per cent.

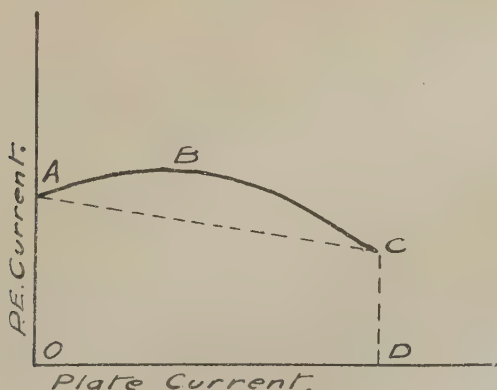
These experiments were deemed sufficient evidence that

the effect is not governed by temperature changes, but by the passage of a current through the metal giving the photo-electric emission. Further evidence of this was, moreover, obtained in the later work, which was extended to a variety of other metals; very interesting results were obtained.

Copper foil was first used, and gave results differing widely from bismuth, but much more closely reproducible. The rise of photo-electric current with increasing plate currents took place very much as with bismuth, but the maxima were attained very much more quickly. Above a certain plate current, however, the photo-electric current began to decrease, and eventually fell below its initial value. With the plate current now cut off, the electrometer readings rapidly passed through the former values, rising to the same maximum and then decreasing to the original value. This cycle could be repeated many times. Such a series of values bears a close resemblance to the curves given by Hallwachs, although in the present case the copper never reached a temperature higher than 250° . A typical curve is given in fig. 2, A.

But still more peculiar was the observation that, starting from the original value of the electrometer reading, the passage of a large plate current carried the photo-electric current directly to the lower value, and from this low value it returned to the initial value by passing through the same maximum as had before been observed.

Fig. 1.



Referring to the small diagram (fig. 1), gradually increasing plate current carries the photo-electric current over the curve A, B, C. The return with plate current cut off is by C, B, A in the course of about 1 hour. Now the

current represented by O D carries the photo-electric current directly and rapidly from A to C ; but with current cut off, the return is again by the route C, B, A. The nature of this cycle, and the fact that it is reproducible within 2 per cent., would appear very difficult to reconcile with an explanation of the phenomenon, based on changes in the gas-content of the metal.

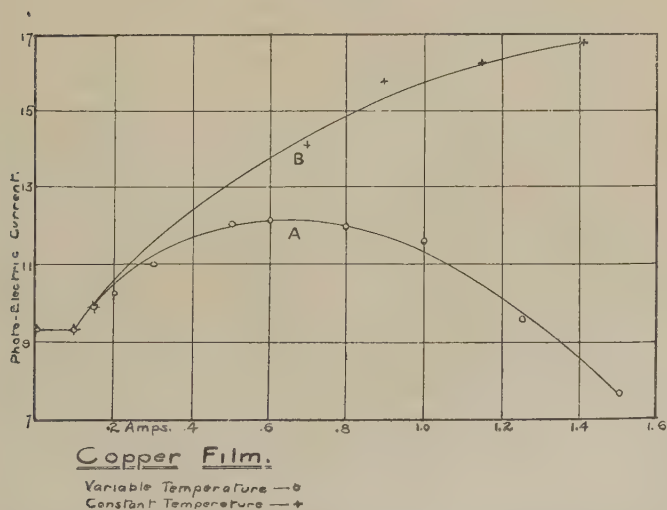
Up to this point, the work was all carried out with polished surfaces, which naturally show considerable differences. In order to eliminate such differences, it was decided to try to work with metallic films formed by evaporation from a hot electrode in a vacuum. To produce such films from electrodes of the metals themselves is a very tedious job, because of the low vapour pressure at the temperature at which it is necessary to work to avoid burning out the electrode. A very easy way of avoiding this difficulty was found. A grid was made of tungsten wire, and this was thinly electro-plated with copper. After baking at a red temperature to eliminate water and absorbed gas, the temperature was run up to just under the melting-point of copper. Thick films on glass could be formed in this way in two or three minutes. The proper temperature could be judged after very little practice. Perfect mirror films of copper were produced of resistance between $\frac{1}{2}$ and 1 ohm for dimensions of 1.2×1 cms. Nickel, gold, and silver were also successfully deposited. To plate silver on tungsten it was found necessary to first plate with nickel. Platinum it was found impossible to plate by this method in the small apparatus in use, on account of the high temperature necessary.

Copper films of this kind showed the same characteristic changes of photo-electric current as had copper foil. Fig. 2 A gives the curve obtained with a film of resistance .4 ohm. As in the case of copper foil, the film could be taken over the cycle A B C B A or A C B A, with deviations of less than 3 per cent. All the copper films gave the same characteristics.

A test of the effect was next made in which temperature changes were practically eliminated. The glass plate with its copper film was cemented to the open end of a glass tube constructed to fit the ground joint of the apparatus. The film was in its usual position close to the electrode, and could be kept at constant temperature by a stream of water against its back surface. The leads were flattened copper and were brought in through the de Khotinsky cement seal. Very striking results were obtained with this arrangement.

The photo-electric current began to increase at very nearly the same film current as before, but the increases were much more marked. Moreover, though increases as high as 70 per cent. were observed, no decrease occurred for currents which had before carried the readings well below the initial value (see fig. 2 B). A further peculiarity was observed when the current was cut off: a decrease of only a few per cent. took place, and the readings then remained constant over a long period. Standing in air or hydrogen for several days had no effect, for, on repumping, the surface showed increases of sensitivity of only 5 per cent. for currents which before produced 70 per cent. increase.

Fig. 2.



The water was next removed from the cooling tube, and current passed through the film, until the plate heated to about 40° C. After cooling and standing for some hours observations were again made. The rise of photo-electric current now made its appearance again, though only to the extent of about 25 per cent. It was apparently impossible for the plate to completely regain its original condition under these experimental conditions; but the indications were that, if heating to a considerably higher temperature were possible, the film would have returned to its first state.

From the experiments just described, it is not unnatural to conclude that the condition produced in a surface by an

electric current is permanent until a considerable rise in temperature takes place.

Of the other metals examined, gold acted in a manner very similar to copper. No attempt was made to follow its characteristic curve closely, but sufficient observations were made to ascertain that it showed a maximum followed by a decrease to well below the initial value. From this low value, however, it returned to the initial value directly, thus differing from copper.

Films of nickel and silver showed characteristics similar to bismuth, but silver proved to be much more rapid in its changes of sensitivity. Nickel showed increases of as much as 50 per cent., but was rather irregular in the return with no current passing. Neither nickel nor silver showed the fall in sensitivity observed in gold and copper for large currents.

As before stated, films of platinum could not be produced in the depositing apparatus used; and, therefore, foil had to be made use of. An attempt was first made to reproduce Ladenburg's observation that successive heatings and coolings of platinum by means of a current finally produces constant photo-electric sensitivity independent of temperature. This effect could not be detected at all for the small temperature variations obtainable in the apparatus in use, the value of the photo-electric current for any plate current being very closely the same after many heatings.

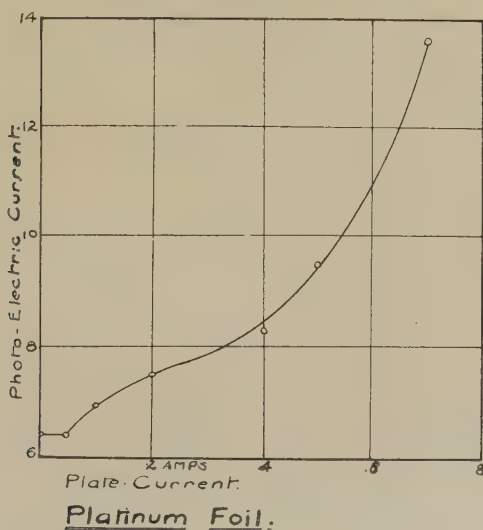
The curve of a run on platinum foil for currents up to 7 amperes is given in fig. 3. It will be observed that the increases are very large, though the temperature could not have risen above 200° C. This statement can be made because of the fact that the soldered connexions of the foil did not fail even with a plate current of 12 amperes. Observations of photo-electric current could not be made above 7 amperes plate current, because above that point the expansion of the leads allowed the foil to touch the electrode.

An attempt was made to discover some co-ordination between the changes of photo-electric effect and contact-difference of potential. Very small changes of contact-potential occurred, which showed no parallelism with the photo-electric changes, possibly due to the fact that air had to be allowed into the apparatus in order to measure the contact difference of potential.

Considering our knowledge of the amounts of gas that are absorbed by metallic surfaces, it is natural to try to base the explanation of phenomena such as have been described on

the variation of the amount and distribution of gas held by the metal. To base the explanation on changes actually produced by an electric current on the electrons and binding forces of the metal itself is very difficult, because of the semi-permanent nature of the changes observed. No theory of metallic conduction has any characteristics which could be used for this purpose. This does not, however, necessarily negative the possibility of an effect of this kind being due to current alone, because theories of conduction do not concern themselves at all with the surfaces

Fig. 3.



of the conductors, and such boundary conditions are all-important for the photo-electric effect. The observations on bismuth warmed without the use of current, and on copper cooled while current was passing, are, I consider, very strong evidence that the effect is not produced by the heating due to the current. There is the possibility that current itself may influence the gas-content of the metal; but, considering all the evidence and particularly the peculiar cycle through which copper can be taken repeatedly and accurately, such an explanation is extremely improbable.

E. T. Whittaker, F.R.S., has recently published a new theory of the quantum mechanism * in the atom, depending on a model in which there is a circular magnetic current.

* Proc. R. S. E. vol. xlii. pt. ii. p. 129.

The quantum relation in the photo-electric effect can be easily deduced from this model. Moreover, since the magnetic current is equivalent to a charged condenser which would be turned with its plane perpendicular to an electric field of force, it is possible that this model might account for Hallwachs' observation of the decrease of photo-electric emission for large currents. But, unfortunately, it has no characteristics which would account either for the complicated changes described above or for their semi-permanent character.

I am, therefore, led into the unsatisfactory position of drawing the conclusion that the changes of photo-electric sensitivity observed must be due to changes produced in the metal by the current passed through it, without in any way being able to approach an explanation of the mechanism by which that result could be produced.

XCIV. *The Resistance of a Hot Wire in an Alternating Air Current.* By R. C. RICHARDS, M.Sc. (Lond.), B.A. (Cantab.), Assistant in the Physics Department, University College, London*.

1. Introduction.

THE resistance of a hot wire in a steady direct current of air has been studied in great detail by many experimenters; and perhaps the most complete treatment of the problem is to be found in a paper of L. V. King†, to whose elegant analysis the reader is referred. The type of relation holding between the resistance and the stream-velocity is by no means simple when considered generally, and is represented graphically by curves of the type shown in fig. 1 (R-V curves). The initial portions of these curves have been studied by Tucker and Paris‡, who came to the conclusion that the drop in resistance produced by a small velocity was proportional to the square of the velocity.

This empirical relation is undoubtedly a very close one, but it must be remembered that the cooling effect of the stream for low velocities is comparable with the radiation heat losses; and therefore the Tucker and Paris relation represents the combined effect of the two cooling factors on

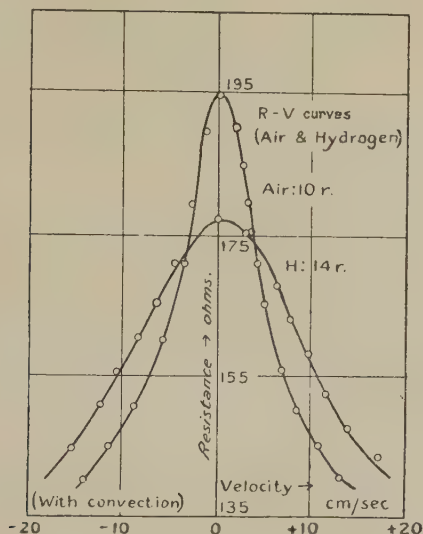
* Communicated by Prof. A. W. Porter, F.R.S.

† King, Phil. Trans. Roy. Soc. ccxiv. A, p. 373 (1914).

‡ Tucker & Paris, Phil. Trans. Roy. Soc. ccxxi. A, p. 389 (1921).

the resistance of the wire. It will be noticed that the resistance reaches a minimum value beyond which an increase in stream-velocity does not further reduce it. Moreover, this minimum resistance is considerably higher than that which the wire would have if its temperature were the same as that of the stream.

Fig. 1.



If the cooling air-current, instead of being direct, were made to alternate so that the velocity at any instant is a simple harmonic function of the time, the general cooling of the wire becomes more complicated, consisting of a steady cooling effect and a superposed oscillatory effect. It is the purpose of the experiments described below to investigate these two effects in their relation to the amplitude and period of the cooling oscillatory draught.

2. Experimental Arrangements.

A standard hot-wire microphone was mounted on the prong of an electrically excited tuning-fork whose amplitude of vibration was maintained at a constant value*, and could be determined by means of a travelling microscope. As the fork was set in vibration the hot wire was thus carried to and fro in an harmonic fashion, and was

* See Note on Amplitude Control.

therefore, in effect, subjected to an harmonic draught. Great care was taken to shield the wire from extraneous draughts.

The wire was balanced electrically in the fourth arm of a Wheatstone net, by which its resistance could be determined. The net was so arranged that the wire was supplied with a constant heating current. Either of two galvanometers could be used, a d'Arsonval or an Einthoven string galvanometer, as the instrument indicating the balance of the Wheatstone net, the former for obtaining the steady drop in resistance and the latter for the oscillatory component. By moving the hot wire along the prong of the fork, it could be made to swing through the different amplitudes, which could be calculated in terms of the end amplitude of the prong and the distance from the end of the fork*.

Sets of readings were taken with various forks of the amplitude of swing of the hot wire and the corresponding steady resistance drop and amplitude of the oscillatory component. This latter was taken to be proportional to the amplitude of swing of the Einthoven galvanometer hair, whose shadow was highly magnified by an optical projector. In all observations on the oscillatory change the steady resistance was first "balanced out" and the galvanometer hair adjusted "out of tune" by the tensioning arrangements.

For very low frequencies—of the order of 1 or 2—the hot wire was caused to vibrate on the end of a long metal rod oscillating under the influence of gravity, like a pendulum.

3. *The Observed Effects.*

It is convenient to classify the various draughts with respect to their frequencies into three groups: (*a*) low-frequency draughts (2 or 3 per second); (*b*) medium frequency draughts (50–60 per sec.); (*c*) high-frequency draughts (120 and over, per sec.), and to deal with the two resistance changes—(α) steady drop, (β) oscillatory change—separately.

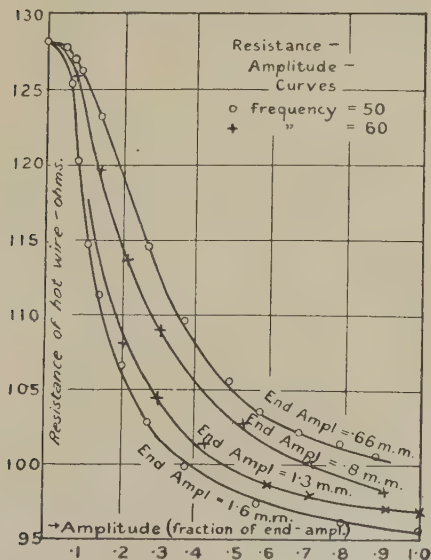
(α) *The Steady Drop.*

- (*a*) A low-frequency oscillatory draught produces no steady drop in the ordinary meaning of the term. The average resistance is lowered, but it returns to its full value twice in every vibration if the imposed draught is at right angles to the direction of the natural convection current, and once per period if the vibration is along this convection current.

* Rayleigh, 'Sound,' 1st ed. vol. i. p. 231 (1877).

- (b) A medium-frequency draught produces a steady drop in resistance which varies as the amplitude increases, as is shown by the graph (fig. 2). It is immediately apparent that this graph is very similar to the steady draught (R - V curves). Moreover, careful examination shows that the region of the curve round about the axis of the amplitude is very nearly parabolic; and thus the steady drop is proportional to the square of the amplitude and therefore to the energy in the oscillatory draught*.

Fig. 2.



- (c) For high-frequency draughts the steady drop follows the same general lines as in (b) above. Curves of precisely the same type were obtained.

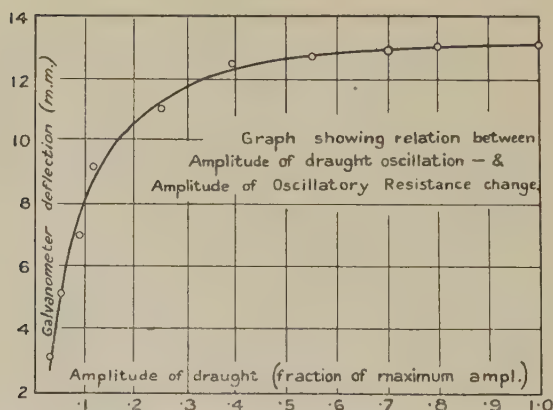
(β) *The Oscillatory Change.*

- (a) The change is almost completely oscillatory. The resistance of the wire evidently keeps at the "equilibrium value" characteristic of the velocity of the draught at any instant. The change in frequency, due to swinging the hot wire in a vertical direction, is brought about by its swinging upwards in its own warm convection current. We thus have cooling on the down journey and recovery on the up.

* Cf. Tucker & Paris, *ibid.* p. 410.

- (b) The amplitude of the oscillatory change is found gradually to increase with increasing amplitude, and to attain a maximum value independent of further increase in amplitude. This is shown in fig. 3. It is to be noted that for small values of the exciting amplitude the oscillatory change is proportional to it*. The frequency of this oscillation could be investigated by means of a telephone, replacing the galvanometer in the bridge arrangement. The note heard is the higher octave of the note given by the tuning-fork, and hence, as one would expect, the frequency is twice that of the exciting vibration.

Fig. 3.



- (c) For high-frequency draughts the oscillatory change becomes very small. It can be detected in a telephone, but it was quite impossible to measure its amplitude by means of the string galvanometer.

4. Theory of the Effects.

We may arrive at a tentative explanation of the above effects by imagining that the resistance of the hot wire will always "follow" (*i. e.*, will always assume the equilibrium value corresponding to) an *increasing* velocity; but its recovery depends upon the rate at which it can draw energy from the external source of current. This is equivalent to saying that the draught can cool the wire down—at the expense of its temperature,—but cannot warm it up again.

Let \bar{R} be the resistance of the hot wire in still air, it being

* Cf. Tucker & Paris, *ibid.* p. 410.

heated by a current produced by a voltage E . Suppose that a current of air be passed over it, reducing its resistance to R ohms, and the draught suddenly cut off.

At the moment of shutting off the draught, the rate of supply of heat is

$$= \frac{dH}{dt} = \frac{E^2}{4 \cdot 2R} \text{ cal./sec.}$$

If the supply of dH calories to the wire raises the temperature $d\theta^\circ \text{C.}$,

$$dH = msd\theta$$

(m = mass of wire, s = specific heat of wire),

but

$$\theta = \text{temperature of the wire} = \frac{R - R_0}{R_0 \alpha}$$

(R_0 = resistance of wire at stream temperature, α = temperature coefficient of resistance);

$$\therefore d\theta = dR/R_0 \alpha.$$

So we have

$$\frac{ms}{dt} \times \frac{dR}{R_0 \alpha} = \frac{E^2}{4 \cdot 2R}$$

or

$$RdR = \frac{E^2 R_0 \alpha}{4 \cdot 2ms} dt;$$

and if the resistance rises from R to R' in a time t , we have

$$\int_R^{R'} R dR = \frac{E^2 R_0 \alpha}{4 \cdot 2ms} \int_{t=0}^{t=t} dt;$$

$$\text{i.e., } R'^2 - R^2 = \frac{E^2 R_0 \alpha}{2 \cdot 1ms} t. \quad \dots \dots \dots (1)$$

If the amount of resistance recovery, *i.e.* $R' - R$, is small compared with R ,

$$R' - R = \frac{E^2 R_0 \alpha}{4 \cdot 2msR} t. \quad \dots \dots \dots (2)$$

The wire being acted on by a draught whose period is T , the wire will have a time $T/4$ for recovery. If R is the resistance of the wire corresponding to $v=0$, the actual time for total recovery would be given by

$$\bar{R} - R = \frac{E^2 R_0 \alpha}{4 \cdot 2msR} \cdot t = \frac{A}{R} t \quad (A = \text{a constant}) \quad \dots (3)$$

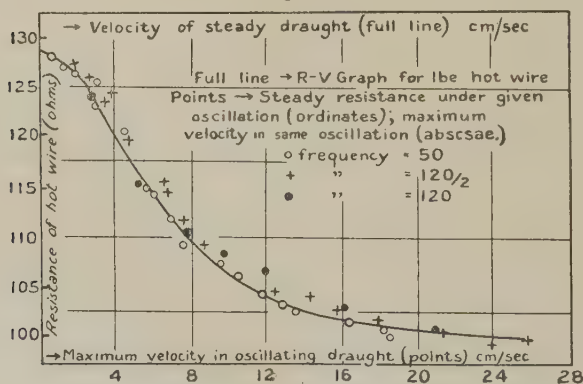
Now if $T/4$ is equal to t or greater than t as given above, R being the resistance corresponding to the maximum resistance in the draught, the wire will completely recover its resistance twice every period.

If $T/4$ is $< t$, the resistance will not recover completely, and a steady drop effect will be produced.

Of course, in practice the time for recovery will be greater than that given by (3), because the wire is not recovering unhindered, as we have assumed, but is still subjected to the decreasing draught in the oscillation. This point must be kept in mind when we come to test the theory quantitatively.

The similarity between the R - V curves (fig. 1) and the Resistance-Amplitude curves (fig. 2) leads one to suspect that the total (steady) resistance drop is one which would be produced by a steady draught proportional to the amplitude of the oscillation for a given frequency, or for any frequency and amplitude proportional to the maximum velocity in the oscillating draught. That the main part of the steady drop in resistance is accounted for in this way is clear from the graph below (fig. 4). The full line is the

Fig 4.



R - V curve for the wire under experiment. The other points are derived from the amplitude-resistance readings for the 50, 60, and 120 forks. The abscissae are the maximum velocities in the oscillating draught, and the ordinates the resistances corresponding to that amplitude from which this maximum velocity has been derived.

It appears, therefore, that the resistance assumed by the hot wire is very nearly the equilibrium resistance corresponding to the maximum velocity in the oscillating draught.

Since this velocity is given by $2\pi na$ (n =frequency, a =amplitude), it follows that, provided $n \times a$ is constant, the steady drop would be the same for oscillations of different frequencies. This is shown in fig. 4. The points for the 50, 60, and 120 forks lie very nearly on the same curve.

Referring to equation (3), it will be seen that the amplitude of the oscillatory change is inversely proportional to R , the lowest resistance produced by the draught, for a given value of T , the period of the imposed oscillation. Plotting this amplitude against $1/R$, the reciprocal of the lowest resistance produced by the draught does not give a straight line, but a curve which degenerates into a straight line for very large values of $1/R$. As has before been pointed out, we cannot expect that equation (3) will do more than generally indicate the relations we find, and this it does satisfactorily. For example, the amplitude of the oscillatory change was seen (fig. 3) to increase with the amplitude of the exciting vibration, and to reach a constant maximum value. Now, as this draught amplitude increases, R , the lowest resistance, decreases (fig. 2), and reaches a constant minimum value: the relation between the amplitude of the oscillatory change and that of the imposed draught is therefore seen to be, in general, in agreement with the simple theory.

Again, fig. 3 shows that the oscillatory change is, *ceteris paribus*, inversely as the frequency. This explains why, for two frequencies, this change is large, and why it practically disappears for high frequencies.

5. Note on Amplitude Control.

A hot wire attached to the prong of a tuning-fork provides a very sensitive amplitude indicator. Referring to fig. 2, if the hot wire be adjusted to work on the region of the curve which is nearly vertical (AB), a small alteration in amplitude will produce a large change in its resistance. The wire being balanced in a Wheatstone net and oscillating at a desired amplitude, will immediately throw the bridge out of balance if the amplitude changes. Steps can then be taken to restore the original amplitude, which will be restored when the bridge indicates balance once more. The writer found that this method would detect a variation in amplitude not observable in a microscope mounted over the vibrating tuning-fork.

6. Summary.

The two resistance changes produced by an alternating air current in a hot wire are examined separately and found to follow, at least approximately, some simple relations. An

elementary "recovery" theory is described, which the writer thinks may be capable of elaboration.

It is hoped that the work may be useful in connexion with the applications of the Tucker hot-wire microphone, as indicating a method of making the instrument sensitive to higher frequencies than has yet been found possible.

The writer's acknowledgements are due to Sir J. J. Thomson, O.M., under whose guidance this work was carried out; and to Dr. Tucker and Mr. Paris for an illuminating discussion on the subject in the summer of 1921.

Physics Laboratory,
University College, London.
February 1923.

XCV. *The Mass-spectra of Chemical Elements.*—Part IV.
By F. W. ASTON, D.Sc., F.R.S., *Fellow of Trinity College, Cambridge* *.

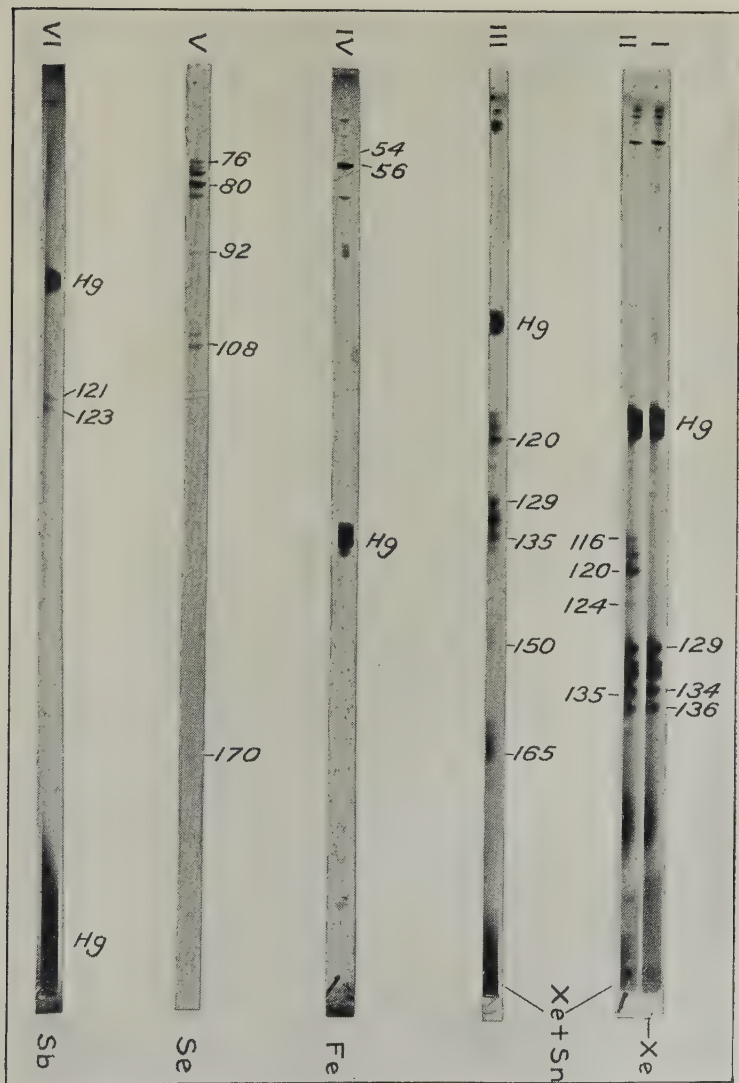
[Plate XIII.]

IN several previous papers† an account of the mass-spectrograph has been given, and the results of analyses carried out by its means described. The following communication deals with similar work continued up to the end of 1922. As already pointed out the work becomes increasingly difficult as the elements under study become less and less suitable for use by standard methods. Many attempts have consequently proved abortive. It is proposed, however, to give some account of both failures and successes, for the results of the former, though negative, often raise points of great interest. As in the previous papers the description of the experiments follows, as far as possible, the order of the experiments themselves.

The general technique has been much the same as that used before except that in most of the more recent work the discharge-tube has been run much "softer." 20 to 30 kilovolt rays are used and the current pushed up to two or more milliamperes. This lessens the risk of coil breakdown and brings the magnetic deflexion of the heaviest elements within the working-range of the existing apparatus. The most important advance has been made quite recently in connexion with the photographic plates employed.

* Communicated by the Author.

† Phil. Mag. xxxix. p. 611; xl. p. 628; xlii. p. 140; xlii. p. 436.



Schumannised Plates.

The action of positive rays on photographic plates, unlike that of light, is purely a surface effect, so that great improvements are to be expected if the concentration of the sensitive grains on the surface is increased. Experiments in this direction have already resulted in very marked success, and it is hoped to give a detailed account of these as soon as a method which gives satisfactory uniformity has been worked out. It will be enough here to state that the process, to which the term "Schumannising" may be applied, consists in partially dissolving the gelatine emulsion away from the plate by means of dilute sulphuric acid. The object is not to remove the gelatine as far as possible, as in the ordinary Schumann plate, but to obtain high surface concentration without making the plate too difficult to handle in the ordinary way. The writer is much indebted to Professor T. R. Merton for information on this very valuable device.

Experiments with Helium.

At the request of Professor McLennan, samples of helium from the Canadian gas-wells were subjected to analysis and carefully examined for the presence of isotopes or other abnormalities. None were observed. This opportunity was taken to endeavour to obtain evidence of the presence of doubly charged helium atoms He^{++} . The alpha rays consist of such particles, and since the potential necessary for the double ionization is of the order 80 volts they must certainly occur in the positive ray discharge-bulb. The importance in the present instance is that the second order line of helium, apparent mass 2.00(0), if obtained on the mass-spectrum would be just separated from the hydrogen molecule line 2.01(5) on the present instrument, and would give an exceedingly accurate and reliable measure of the relative masses of the two bodies. Many plates were taken under a great variety of conditions, but in no case could a line be detected in the expected position near the H_2 line. The most probable explanation seems to be that the sphere of action of a particle with an ionization potential of 80 volts is so large that a negligible percentage, if any, of the doubly charged helium nuclei are able to pass the slit system and the analysing fields without collision with, and capture of, a stray electron.

NICKEL (At. Wt. 58.68).

The obvious compound to use in investigating this element was Nickel Carbonyl. In the earlier experiments of Sir J. J. Thomson with this substance it had been found exceedingly troublesome to deal with. On entering the discharge-tube it immediately decomposed, and the metal deposited on the walls as a black mirror soon prevented normal discharge altogether. In the present experiments this difficulty was overcome to a sufficient degree by diluting the vapour of the carbonyl with CO_2 and running the maximum safe current through the tube to lessen the necessary exposure. The mass-spectra obtained, though not strong enough for reproduction, were quite easy to interpret and showed conclusively that nickel consists of two isotopes 58 and 60. The intensity relation between their lines agrees well enough with the mean atomic weight quoted and supplies a simple explanation of the long discussed anomaly of the atomic weights of nickel and cobalt. The two nickel lines when measured against mercury lines of the third and fourth order as standards show no measurable deviation from the whole number rule.

Experiments with Metallic Chlorides.

In the cases of many out of the large number of elements yet to be analysed the only stable and easily obtainable compounds with a reasonable vapour pressure are chlorides. This is unfortunate in many ways. In the first place most of these chlorides have a violent action on rubber tap grease. In the present form of apparatus the vapour has to pass several stopcocks and it is quite possible that the most active ones are entirely decomposed and never reach the discharge at all. Even if this difficulty were removed by alteration of the admission arrangements there still remains a more serious one. This is that the passage of the discharge in such compounds must inevitably release free chlorine. The latter can, and apparently does, form volatile compounds with practically every element used in the construction of the apparatus, including the aluminium of the electrodes and the silicon of the glass. The result is a perfect maze of lines filling every successive unit place and effectually screening any clear vision of the lines of the element under observation. This effect is enormously exaggerated by the proclivity of chlorine to form hydrogen addition products, and also by its isotopic constitution since for every type of combining particle there will be two lines due to the monochloride, three to the dichloride, four to the trichloride, etc.

Thus titanium chloride gave spectra of great complexity but perfectly useless for identifying the isotopes of the metal, even if their lines were present, since all the units from 44 to 52 were filled by lines of various intensities. There was a group of lines 82-86, the last four of which were very strong. Now titanium has an atomic weight 48.1, so one might easily have been led to the identification of these as its monochlorides and hydrochlorides. Fortunately, however, this characteristic group had been obtained before with tin tetrachloride, a compound of similar chemical properties. It is probably due in the main to CCl_2 and CHCl_2 derived from the action of the metallic chloride on the tap grease. If the reader will refer back to plate vii., *Phil. Mag.* vol. xlii. the group will be seen plainly near the strong Hg band on Spectrum II.

Chromyl chloride was even more hopeless for its action on tap grease and wax was so rapid as to make it quite unworkable.

Experiments with Lead Ethide and Zinc Methide.

When the apparatus had been thoroughly cleaned from the effects of the chlorine compounds an attempt was made to obtain the lines of lead by the use of its volatile tetraethide. The writer is indebted to Sir W. Pope for a sample of this compound and also for the titanium chloride already mentioned. The importance of settling the much discussed isotopic constitution of ordinary lead is obvious, but unfortunately the experiments gave no results of any value. No signs of lines were visible in the expected region although very long exposures were resorted to. If, as is possible, this negative result was caused by the abundant liberation of carbon and hydrogen compounds from the decomposing ethide, the difficulty might be reduced by the use of the simpler methide. The experiments will be repeated when this compound is available, but hope of success in this direction has been already discounted by some later experiments with zinc methide which failed entirely to give the zinc lines. The values of the latter are already known from the fine work of Dempster* but confirmation by the mass-spectrograph would have value, particularly in connexion with the accuracy of the whole number rule.

On introducing the vapour of zinc methide into the discharge-tube only one new line made its appearance. This

* A. J. Dempster, *Phys. Rev.* xx, no. 6, Dec. 1922.

one was quite obvious and at a point corresponding to mass 127. It is doubtless due to the presence of traces of iodine derived from the methyl iodide used in the manufacture of the methide. When one considers that the sample was a perfectly colourless one and described as chemically pure, this is a striking illustration both of the selective quality and the extraordinary delicacy of analysis by positive rays.

Further Experiments with Xenon.

It has been pointed out* that whereas the atomic weight of xenon calculated from Moore's determination of its density is 130.2†, that deduced from the results of the mass-spectrograph is about one unit higher. No great accuracy is claimed for the latter method but the discrepancy is rather larger than is to be expected and it has been suggested that the density result might be really too low owing to the possible presence of krypton as an impurity.

A welcome opportunity to put this point to the test was afforded during the recent visit to Cambridge of Dr. R. B. Moore, who kindly brought over from Washington a small sample of the original xenon which had been used for the density determination. Several mass-spectra were obtained with this gas, but although considerable exposures were given no definite evidence of the krypton group of lines could be detected. Since krypton is very sensitive to positive ray analysis this result shows that it could not possibly have been present to the extent required to account for even a small fraction of the discrepancy, which therefore remains unexplained.

These experiments had indirect results of importance, for the residual xenon in the discharge-tube gave excellent lines on some of the first experimental schumannised plates. These not only established a point of fundamental importance in connexion with the element, tin, considered below, but confirmed beyond doubt the presence of two weak xenon isotopes 128, 130 previously suspected. Owing to the completely changed characteristics of the plates these could now be clearly distinguished on the original negatives, and may be seen each side of the strong 129 line on Spectra I and II of the plate.

More recently during a search for an inert element of high atomic weight in the atmosphere, a full account of which

* F. W. Aston, 'Isotopes,' p. 114.

† H. E. Watson, Trans. Chem. Soc. p. 836 (1910); R. B. Moore, *ibid.* p. 2181 (1908).

will be published later, two new components of xenon were discovered at 124, 126. These give very faint lines only distinguishable on spectra in which the ordinary xenon lines are enormously over exposed. There is every reason to suppose that they are due to two isotopes of xenon present in exceedingly small quantities, probably less than one-tenth per cent. of the whole. The line at 126 appears slightly stronger than that at 124. As all the possible reference lines were hopelessly over-exposed these numerical values are only approximate.

TIN (At. Wt. 118.7).

In some earlier experiments with tin tetrachloride the complex nature of the element was suspected but not conclusively proved, it has now been satisfactorily demonstrated by the use of tin tetramethide, a specimen of which was kindly supplied by Sir W. Pope. The first experiment with this substance was perhaps somewhat fortunate and the spectra obtained on this occasion present features of great interest. Some of them are reproduced on the plate, Spectra I, II, and III. Spectrum I was taken before the tin compound was introduced. Its principal lines are those of xenon residual from the previous experiment and mercury. Spectra II and III show the new lines due to tin and its compounds. The element is evidently highly complex, it has isotopes 116, 117, 118, 119, 120, 122, 124 and a faint possible eighth at 121. The order of intensity can be seen on the plate and is given in the table at the end of the paper. The intensities are such as to preclude the possibility of any of the lines, except the very faint one at 121, being ascribed to hydrogen addition products. Satisfactory confirmation of the isotopic nature of the lines is provided by the reproduction of the entire complex group with identical intensity relations, 15, 30 and 45 units higher up the mass-scale, due obviously enough to SnCH_3 , $\text{Sn}(\text{CH}_3)_2$, and $\text{Sn}(\text{CH}_3)_3$. A reference to the mass-spectrum obtained with tin tetrachloride and reproduced in the plate already mentioned*, shows that the tin lines were really obtained then, but the disclosure of the fainter components lying between pairs of stronger ones has only now been made possible by the remarkable improvement in definition given by the new type of plate.

Measurements of the lines of tin show that while their masses are integral within experimental error with regard to

* Plate vii. *Phil. Mag.* vol. xlii.

each other, yet when compared with the other lines on the plate they give values *less than whole numbers by 2 to 3 parts in 1000*. This remarkable result would certainly have been suspected of being an experimental error had it not been for the fortunate presence of the xenon lines on the plate, and the appearance of the lines of tin monomethide amongst them. There are two strong xenon lines at 134, 136 which have been compared with the lines of mercury in previous experiments, and there is no reason to doubt that they are integral to about 1 in 1000. The strongest tin monomethide line $\text{Sn}^{120}\text{CH}_3$ should lie evenly between these two lines. It is very clear that it does not do so, but, on the contrary, is shifted so far to the left as to coalesce partially with Xe^{134} so that the latter appears broadened. This marked asymmetry is repeated in another part of the plate in Spectrum III taken with a stronger magnetic field.

It seems impossible to imagine any instrumental defect which could give rise to this shift. There appears, therefore, to be no escape from the conclusion that tin and xenon cannot both obey the whole number rule. It was realized and emphasized* that this rule was not to be expected to hold with mathematical exactness owing to the packing effect, but it is very surprising that elements only differing by three units in atomic number should show so large a divergence. It seems probable that the divergence from the mean ($O=16$) is greater in the case of tin than in that of xenon, but since the arithmetic sum of the two (supposing them to be of opposite signs) is only about three times the experimental error, satisfactory settlement of this point will have to be deferred till an instrument of higher precision is available.

IRON (At. Wt. 55.84).

This element was investigated by means of its volatile carbonyl. A sample of this somewhat rare compound was obtained from the Chemical Department through the kindness of Mr. W. H. Mills. The experimental treatment was the same as that described above for the nickel compound, but the difficulties were more pronounced and the results not so definite. One of the spectra obtained is reproduced, Spectrum IV on the plate. The only line which can be ascribed with certainty to iron is the one at 56. The faint line at 54 may possibly be an isotope, but this is by no means certain. Thirteen independent measurements of the principal line relative to other lines on the plate gave values

* Phil. Mag. xxxix. p. 624.

of its mass which were very consistent and had a mean of 55.94. This only differs from the chemical value by 2 in 1000 so that it is by no means unlikely that iron is a simple element.

Experiments with Cadmium and Thallium.

The boiling point of cadmium, 778°C ., is not excessively high so it was hoped that its mass-spectrum would be obtained if the metal was volatilized inside the discharge-tube. The method adopted for carrying this out was to lower a quartz glass vessel containing a small quantity of the substance into the path of the cathode ray beam by means of a winch. By careful adjustment of the position of the vessel it could be raised to any desired temperature up to a bright red heat. The cadmium was vaporized without the least difficulty and immediately condensed as a bright mirror on the cooler walls of the tube, but the vapour pressure could not have been high enough to affect the discharge for the optical spectrum showed no cadmium arc lines. The mass-spectra obtained showed no signs of lines in the expected region so the experiment failed to achieve its object.

It is interesting to note that mercury was completely eliminated from the discharge almost instantaneously when the cadmium volatilized. Its lines vanished entirely from the mass-spectra and did not reappear so long as the cadmium mirror remained on the walls of the discharge-tube. This method of eliminating every trace of mercury may be of considerable value in the future. In the present instance advantage was taken of it to attempt the analysis of thallium. This element has an atomic weight of 204 so that its lines would certainly be obscured by those of mercury except under these special conditions. Thallium chloride, which is fairly volatile, was therefore introduced and volatilized, but although the lines of chlorine appeared there was no sign of any that might be due to thallium. It is possible that the cadmium layer removes the vapour of the element as effectively as it does that of mercury.

SELENIUM (At. Wt. 79.2).

Previous experiments with selenium hydride* had been completely unsuccessful, but on volatilizing the element itself by the method described above conclusive results were immediately obtained. Spectrum V on the plate shows that selenium is characterized by five strong lines 76, 77, 78, 80, 82 and a very faint sixth at 74. The true isotopic nature of

* Phil. Mag. xlii. p. 140.

this group is beautifully brought out by its repetition at a position 12 units higher on the mass-scale due to CSe and 28 units higher due to COSe. Some of the faint lines of the complex group CSe₂ may also be distinguished on the right. The evidence of the isotopic constitution of selenium is therefore exceptionally definite and satisfactory. The order of intensity of the lines can be seen on the spectrum and is given in the table; it agrees reasonably well with the chemical atomic weight. It will be noticed that no fewer than three of the isotopes of selenium 78, 80, 82 are isobaric with those of krypton.

Experiments with Tellurium and Beryllium.

The success with selenium raised hopes for tellurium which had also been attacked previously without result*. Pure tellurium element was volatilized but no lines attributable to it could be seen on the mass-spectrum. This failure is probably due to its high boiling point and consequent low vapour pressure. A second attempt was made using the more volatile tellurium chloride, but again, though chlorine was present in abundance, there was a complete failure to obtain the lines of tellurium.

Beryllium acetate was introduced, but its volatilization was accompanied by immediate decomposition and a deposit of white oxide appeared. No evidence of the line of beryllium could be seen at the expected position 9, G. P. Thomson's positive ray observations, however†, and the latest value 9.018 obtained for its atomic weight‡ leave little doubt as to its simple constitution.

ALUMINIUM (At. Wt. 26.96).

Aluminium has long been suspected of being a simple element on account of the closeness of its chemical atomic weight to an integer. This view is further supported by the rule, now known to be obeyed in so many cases, that elements of odd atomic number have few isotopes, never more than two, and that these isotopes have odd atomic weights. The occasional appearance of a faint line at 13.5 on mass-spectra taken when chlorine was present in the discharge has been ascribed to Al⁺⁺ derived from the electrodes§.

During the experiments on tellurium chloride the chlorine liberated attacked the electrodes to an unmistakeable extent. In fact the slit in use was ruined by the corrosion. It is therefore perfectly certain that volatile aluminium chloride

* *Loc. cit.*

† G. P. Thomson, *Phil. Mag.* xlii. p. 857.

‡ Honigschmid and Birckenbach, *Ber.* lv. B, pp. 4-12 (1922).

§ *Phil. Mag.* xl. p. 633.

must have been present in considerable quantity during the exposures. The indication of its presence was equally strong on the mass-spectra obtained. The line at 27, usually very much weaker than that at 28, was very intense and its second order line easily visible at 13.5. Furthermore, strong groups of lines appeared with their first units at 62 and 97. The intensities of the lines in these groups show that they are due to the mono- and dichlorides of bodies having masses 27 and 28. The latter may be an atom of Si^{28} or a molecule of CO but the only feasible origin of the former is an atom of aluminium. It is therefore reasonably certain that this element consists mainly of atoms of mass 27, and since there is no evidence of atoms of lighter mass the chemical atomic weight leads definitely to the conclusion that it is simple. Measurements of the line 13.5 show no measurable deviation from the whole number rule.

Some valuable evidence on the constitution of chlorine was obtained from these experiments at the same time. One of the spectra showed the lines 35, 36, 37, 38 exceedingly intense, with no vestige of a line at 39. It is therefore certain that the hypothetical isotope 39 does not exist in any appreciable quantity.

ANTIMONY (At. Wt. 120.2 (?)).

The failure to obtain the spectrum of antimony from its hydride has already been described*. In connexion with the successful analysis now achieved the writer wishes to record his most hearty thanks to Professor G. T. Morgan, who prepared a sample of antimony methide specially for the purpose and also supplied the samples of tellurium chloride and beryllium acetate used in the experiments just described. The antimony methide vapour was introduced mixed with CO_2 and gave exceedingly good results at once. One of the spectra obtained is reproduced in Spectrum VI on the plate. The element is characterized by two strong lines 121, 123, the former being slightly the more intense. When sufficient exposure is given similar pairs appear 15 and 30 units higher on the mass scale (*c.f.* Tin, p. 939) due to the mono- and dimethide respectively. Faint companions have been seen also at 122, 124, but from their irregular intensity relations it is practically certain that these are due to hydrides. These results show that antimony is a complex element consisting of two isotopes, 121 and 123. Measurement of the lines shows no appreciable deviation from the whole number rule so that it is quite certain that the international atomic weight quoted above is much too

* *Phil. Mag.* xlii. p. 141.

low. On the other hand the value 121.77 recently obtained by Willard and McAlpine* is in agreement with the results of the mass-spectrograph.

Table of Isotopes and the Whole Number Rule.

So long as only one element, hydrogen, showed measurable deviation from the whole number rule it was reasonable to identify the whole numbers with the true masses of the isotopes on the oxygen scale. Now that further exceptions have been discovered—tin, and probably iron—this identification cannot be continued. No useful purpose will be served by introducing the fractional values until these can be obtained with much greater accuracy. In the following table they are omitted and the *nearest* integer given. These

Table of Elements and Isotopes.

Element.	Atomic Number.	Atomic Weight.	Minimum number of Isotopes.	Mass-numbers of Isotopes in order of intensity.
H	1	1.008	1	1
He	2	3.99	1	4
Li	3	6.94	2	7, 6
Be	4	9.0	1	9
B	5	10.9	2	11, 10
C	6	12.00	1	12
N	7	14.01	1	14
O	8	16.00	1	16
F	9	19.00	1	19
N	10	20.20	2	20, 22
Na	11	23.00	1	23
Mg	12	24.32	3	24, 25, 26
Al	13	26.96	1	27
Si	14	28.3	2	28, 29, (30)
P	15	31.04	1	31
S	16	32.06	1	32
Cl	17	35.46	2	35, 37
A	18	39.88	2	40, 36
K	19	39.10	2	39, 41
Ca	20	40.07	2	40, 44
Fe	26	55.84	(1)	56, (54)?
Ni	28	58.68	2	58, 60
Zn	30	65.37	4	64, 66, 68, 70
As	33	74.96	1	75
Se	34	79.2	6	80, 78, 76, 82, 77, 74
Br	35	79.92	2	79, 81
Kr	36	82.92	6	84, 86, 82, 83, 80, 78
Rb	37	85.45	2	85, 87
Sn	50	118.7	7 (8)	120, 118, 116, 124, 119, 117, 122, (121)
Sb	51	121.77	2	121, 123
I	53	126.92	1	127
X	54	130.2	7 (9)	129, 132, 131, 134, 136, 128, 130, (126), (124)
Cs	55	132.81	1	133
Hg	80	200.6	(6)	(197-200), 202, 204

(Numbers in brackets are provisional only.)

* Willard and McAlpine, Jour. Am. Chem. Soc. xliii. p. 1085 (1921).

integers are provisionally called "mass-numbers." The mass-number may be taken to represent the number of protons in the atom for it seems exceedingly unlikely that the packing effect will ever throw the mass out as much as half a unit. At the same time such a possibility must not be entirely ignored. The table gives a complete list of all those elements whose isotopes have been determined by any of the positive ray methods up to the present.

In conclusion the writer wishes to repeat his acknowledgement to the Government Grant Committee of the Royal Society for part of the apparatus employed in this research.

Summary.

Further experiments with the mass-spectrograph are described by which the constitution of six more elements Ni, Sn, Fe, Se, Al, Sb has been determined.

Two new isotopes of xenon have been discovered and evidence obtained excluding 39 from the isotopes of chlorine.

Deviations from the whole number rule have been observed in the case of the masses of the isotopes of tin compared with those of xenon.

A complete table is given of the isotopes of the thirty-four elements whose constitution has so far been determined by the methods of positive rays.

Cavendish Laboratory,
Cambridge, Feb. 1923.

XCVI. *The Hot-Wire Inclinometer: its Sensitivity in Air and in Carbon Dioxide.* By J. S. G. THOMAS, D.Sc. (Lond. and Wales), A.R.C.Sc., A.I.C., Senior Physicist, South Metropolitan Gas Company, London*.

Introduction.

A form of hot-wire inclinometer comprising a pair of fine heated platinum wires arranged parallel and close to one another within an enclosure has been recently described by the author†. The wires constitute two arms of a Wheatstone bridge, and the deflexions of the galvanometer depend upon the variation of the thermal conditions of the respective wires as the plane of the wires is rotated about a

* Communicated by the Author.

† Proc. Physical Soc. vol. xxxii. p. 291 (1920).

horizontal axis, either in, or at right angles to their plane. The dependence of the sensitivity of the inclinometer upon the distance separating the wires was discussed in a subsequent paper *. Humphrey † showed that the sensitivity was increased when the air surrounding the wires was replaced by carbon dioxide. Previous experience with fine heated platinum wires surrounded by various gases, made it appear improbable that this conclusion could be correct under all conditions, and the present investigation was undertaken to ascertain the criteria for greater sensitivity in one or other of the two media, air and carbon dioxide.

Experimental Results and Discussion.

Two series of experiments were carried out. In either series the inclinometer was composed of two fine heated platinum wires of diameter 0.10 mm. Particulars of the

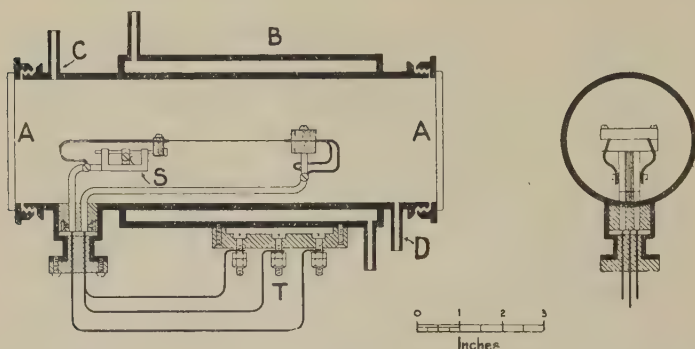


Fig. 1.

preparation of the wires prior to use have been given in the papers already referred to. In the first series, the wires were mounted in a large brass cylindrical chamber, 25 cm. in length and 7.6 cm. in diameter, the ends being closed by glass plates, A, as shown in fig. 1. In the second series the enclosure was a narrow brass tube of the same length, but only 6 mm. in diameter. Wider chambers were provided at the end of this tube for the purpose of mounting the wire. In each case the enclosure was provided, as shown in fig. 1, with a jacket B, through which tempered water maintained

* Phil. Mag. vol. xlii. p. 940 (1921).

† Proc. Physical Soc. vol. xxxiii. p. 190 (1920-1921).

throughout at $15^{\circ}\text{C.} \pm 0^{\circ}\cdot 5$ flowed. The bridge arrangement and the galvanometer sensitivity remained throughout the same. The wires were mounted parallel to one another at a distance apart equal to about 1.5 mm., and when heated were maintained just taut by the spring device S as described in a previous communication*. The ends of the wires were connected to terminals shown at T. The various points were made tight by means of sealing-wax, and the enclosure could be filled with either air or carbon dioxide as desired, through the tube C. D served as outlet, and was connected to a water-pump for the purpose of exhausting the chamber. Both inlet and outlet tubes were provided with taps and calcium chloride tubes for maintaining a dry atmosphere within the chamber. The chamber was mounted so as to be capable of rotation about a horizontal axis parallel to the plane of the wires, the rotation being indicated on a divided circle, and the pressure within the chamber was indicated by means of a mercury manometer.

Particulars of the wires are set out herewith:—

Length of each wire 7.0 cm.

Distance apart of wires 1.5 mm.

Temperature coefficient of wires . . 0.003226.

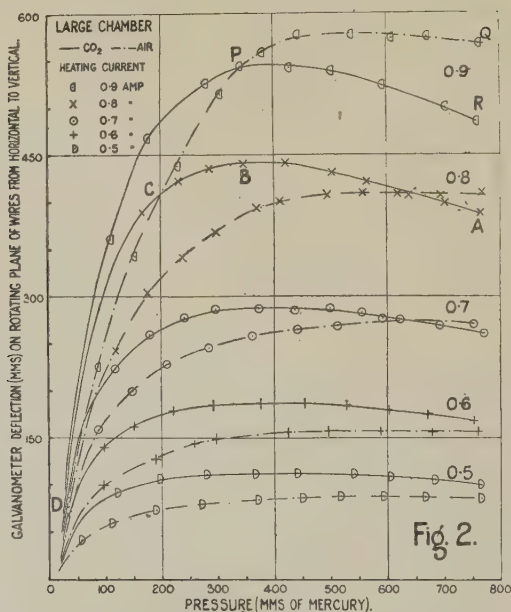
Resistance of each wire at 15°C. . . 0.934 ± 0.003 ohm.

With the plane of the wires horizontal and the bridge-current flowing through the wires in series, the bridge was balanced, the fixed arm of the bridge being throughout maintained at 1000 ohms. The galvanometer deflexion was then determined on rotating the plane of the wires from the horizontal to the vertical position, the current in the bridge being adjusted to its previous value.

The results obtained with the large chamber, when using different bridge-currents, and for various values of the pressure in the chamber are shown in fig. 2. The currents corresponding to the various pairs of curves were, 0.5, 0.6, 0.7, 0.8, and 0.9 amp. respectively. It will be observed that at atmospheric pressure (760 mm.), for equal values of the bridge current, there is a relatively small difference in the deflexion for 90° rotation, according as the medium surrounding the wires is air or carbon dioxide. Moreover, while for the lower values of the heating current, the sensitivity of the inclinometer is somewhat greater in the case of carbon dioxide, the ratio of the respective sensitivities (CO_2/Air) is very much less than that to be anticipated from

* Phil. Mag. vol. xliii. p. 278 (1922).

Humphrey's experiments *. With increase in the value of the heating current, at atmospheric pressure, the deflexion on rotation of the plane of the wires from the horizontal to the vertical becomes greater for air than for carbon dioxide, as shown by curves corresponding to currents of 0.7, 0.8, and 0.9 amp. The relative order of magnitude of the respective sensitivities is thus inverted with increase in the heating current. Attention may here be directed to two other outstanding features of the curves shown. In the case of air, with decrease of pressure in the chamber from atmospheric,

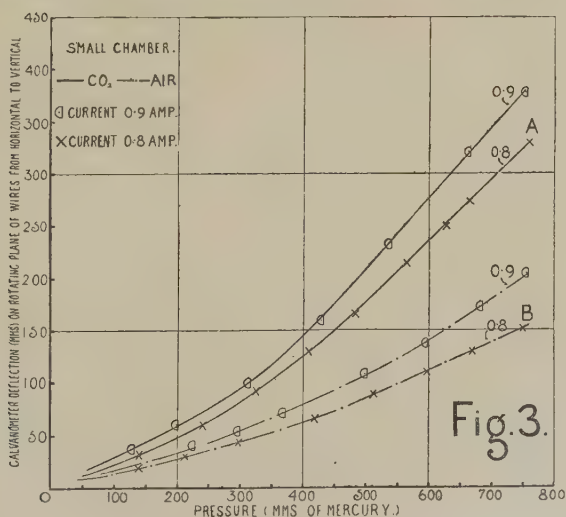


there is initially very little, if any increase of galvanometer deflexion. With carbon dioxide on the other hand, the initial decrease of pressure is in all cases accompanied by a very marked increase of galvanometer deflexion as shown, *e.g.*, by the points A and B for the curve corresponding to 0.8 amp. Compared with the ultimate very rapid decrease of deflexion accompanying a decrease of pressure, such increases are, however, comparatively small in all cases (*see, e.g.*, portion CD of curve just referred to). It will be observed that for all the respective values of the bridge

* *Loc. cit.* p. 191.

current, provided the pressure in the chamber is sufficiently reduced, the sensitivity of the inclinometer in carbon dioxide is somewhat greater than that in air and the ratio of the respective deflexions increases as the pressure is reduced.

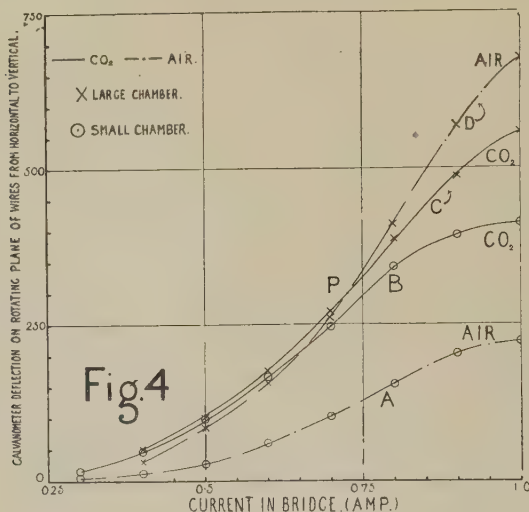
Representative curves in which the galvanometer deflexions on rotation of the plane of the wires from the horizontal to the vertical in either air or carbon dioxide respectively are plotted as ordinates against the corresponding pressures in the chamber as abscissæ, are given for the narrow chamber of diameter 6 mm. in fig. 3. Currents of 0.8 and 0.9 were employed in the curves shown. The curves differ in character



very considerably from those shown in fig. 2. Thus, for example, for a current of 0.8 amp. and a pressure of 760 mm. in the case of the large chamber, the deflexions with the wires in air or carbon dioxide are very little different, the former being slightly the greater. In the case of the small chamber, however (see curves A and B), the corresponding deflexion with the wires in carbon dioxide is more than double of what it is when the wires are surrounded by air. Moreover, in fig. 3, for any fixed value of the bridge-current, the deflexion corresponding to any definite pressure is throughout greater in the case of carbon dioxide than in the case of air, while in general, in fig. 2, this is the case only for comparatively low pressures for bridge currents equal to 0.8 and 0.9 amp.

The values of the deflexions on rotation of the plane of

the wires from the horizontal to the vertical are plotted in fig. 4, as ordinates against the respective values of the bridge current as abscissæ, the pressure being throughout adjusted to 760 mm. of mercury. Curves A and B refer to the small chamber, and curves C and D to the large chamber. It is seen that at this pressure the greatest sensitivity of the inclinometer is afforded when the wires are enclosed in a *large* chamber containing *air* (curve D). In such a chamber the sensitivity in both air and carbon dioxide is greater than that characterizing the respective sensitivities



in a chamber such as that employed by Humphrey, in which an inversion of this order of relative sensitivities occurs (curves A and B). Attention may here be directed to the inversion of the relative magnitudes of the respective sensitivities in air and carbon dioxide when the wires are enclosed in the large chamber, and the value of the current is altered. As shown by the point P in fig. 4, in this chamber, for values of the heating current below about 0.73 amp., an enclosure containing carbon dioxide affords the greater sensitivity; above this value of the bridge-current, the greater sensitivity is obtained when the large chamber is filled with air. In the small chamber, no such inversion of the relative magnitude of the respective sensitivities occurs.

All the results may be readily interpreted as follows :— In the large chamber the differential thermal effect experienced by the wires on rotation is conditioned partly by convection effects, and partly by conduction and radiation effects. In the small chamber, convection effects are almost entirely eliminated. For the present purpose radiation effects can be neglected, and attention confined entirely to convection and conduction effects under the various conditions of the experiments.

Consider first the curves corresponding to a current of 0.9 amp. in fig. 2. For pressures less than 350 mm. of mercury (point P) in the large chamber, an atmosphere of carbon dioxide affords the greater sensitivity. This result is analogous to those shown by the curves for the small chamber in fig. 3, and indicates that as the pressure is reduced below about 350 mm. of mercury with a heating current equal to 0.9 amp. differential effects due to convection become relatively diminishingly unimportant compared with differential conduction effects in the chamber. For lower values of the heating current, the pressures corresponding to the intersection of the respective curves become higher, and for heating currents of 0.5 and 0.6 amp., the respective curves for air and carbon dioxide would presumably intersect at points corresponding to pressures greater than atmospheric.

The differential convection effect is conditioned by a variety of factors as the pressure in the large chamber is reduced. Among these are included : (a) the higher temperature of the wire, (b) the diminished density of the gas in the chamber, and (c) the increased velocity of the free convection current from the wires due to (a) and (b). Attention has already been directed to the different slopes of the portions Q P and R P of the curves in fig. 2 for air and carbon dioxide as the pressure in the large chamber is reduced below 760 mm. Interpreted in the light of the formulæ given by King* and by Langmuir† for the free convection loss from a fine heated platinum wire, these results indicate that for air, over the appropriate range of pressures, the value of the product $S\sigma V$, where S is the value of the specific heat of air at constant volume, σ the density of the gas, and V the velocity of the free convection current, is practically constant. For carbon dioxide on the other hand, the value of the product increases as the pressure in the chamber is reduced, the value of V increasing at a greater rate than $S\sigma$ decreases.

* Phil. Trans. A, vol. 214, p. 381 (1914).

† Phys. Rev. vol. xxxiv. p. 401 (1912).

It will be clear that the explanation of the characteristics of the various curves for the large chamber in fig. 2 is tantamount to the following. For low pressures and (or) small values of the heating current, the differential thermal effects experienced by the wires are conditioned principally by considerations of conduction losses from the respective wires. For larger values of the heating current and comparatively high pressures, differential convection effects become increasingly important. The respective thermal conductivities of air and carbon dioxide at 0°C. are 5.22×10^{-5} and 3.07×10^{-5} c.g.s. units respectively. For the same small values of the heating current, therefore, the wires when surrounded by air in the large chamber will be colder than will be the case when carbon dioxide is the medium contained in the chamber. It may be anticipated, therefore, that the differential thermal effects are under these conditions less in air than in carbon dioxide. In like manner, for low values of the pressure in the large chamber, the temperature of the wires surrounded by air will be lower than is the case when the chamber is filled with carbon dioxide.

It has been previously shown that dissipation of heat from the hot wire to the surrounding medium occurs directly through a thin layer of stagnant gas surrounding the wire*. As the temperature of the wire is increased, the temperature gradient in, and the thermal conductivity of, this stagnant layer increases. Calculation shows that the thermal conductivity of carbon dioxide increases much more rapidly with temperature than does that of air. Thus, calculating the respective values of the conductivities of carbon dioxide and air at 360°C. , 690°C. , and 1060°C. , (corresponding to the points R, P, and Q respectively in fig. 6, on page 955 later) by extrapolating O. E. Meyer's formula $K = 1.603 \eta_t c_v$, employing Sutherland's formula for calculating η_t we find:—

Temperature (0°C.)	Thermal Conductivity.		Ratio $\frac{K_t}{K_0}$	
	Air.	Carbon Dioxide.	Air.	Carbon Dioxide.
0°	5.22×10^{-5}	3.07×10^{-5}	1	1
360°	8.7	7.6	1.7	2.5
690°	11.4	10.4	2.2	3.4
1060°	13.8	12.9	2.6	4.2

It will be seen that while the respective thermal conductivities of air and carbon dioxide increase rapidly with

* Phil. Mag. vol. xxxix. p. 534 (1920).

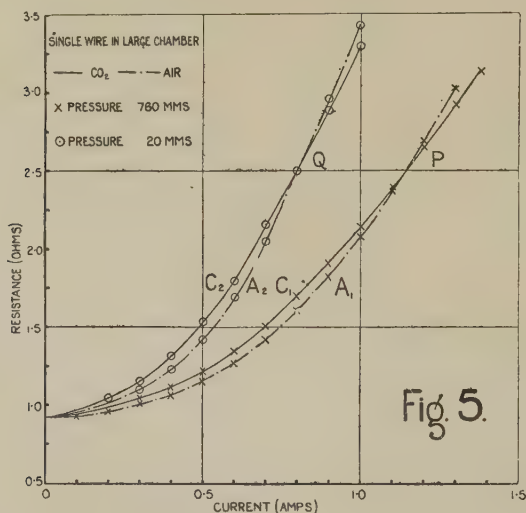
increase of temperature, the rate of increase in the case of carbon dioxide is very much greater than in the case of air. So far as experimental evidence is available *, it is probable that as the temperature of the wires is increased, the ratio of the heat dissipated by conduction to the total heat dissipated from the wires increases. This effect, combined with the greater relative increase in the thermal conductivity of the stagnant layer surrounding the wires in the case of carbon dioxide, leads to the conclusion that with rise of temperature the proportion of heat lost by conduction increases more rapidly in the case of a wire surrounded by carbon dioxide than in the case of one surrounded by air. Alternatively, we may say that, with rise of temperature, the proportion of heat lost by convection increases more rapidly in the case of air than in the case of carbon dioxide. It is therefore to be anticipated that under conditions where differential thermal effects experienced by the wires are determined principally by convection currents, *i. e.*, for large values of the heating current and moderate or large values of the pressure in the chamber, the sensitivity of a hot wire inclinometer in which the wires are surrounded by air would be greater than would be the case with carbon dioxide surrounding the wires. This is in accordance with the results corresponding to the portions Q P and R P of the curves corresponding to a bridge-current of 0.9 amp. in fig. 2. A similar result is shown by the corresponding portions of the curves for 0.8 and 0.7 amp.

The correctness of the view advanced in the preceding paragraph was readily verified by determining the resistance of one of the wires surrounded by either air or carbon dioxide in the chambers. This was done by measuring, by means of a potentiometer, the voltage drop across the wire when a known current was maintained in the wire. The potentiometer readings were calibrated by a Weston cell standardized at the National Physical Laboratory. The pressure within the chamber was adjusted throughout to one or other of the values 760 mm. or 20 mm. of mercury respectively in two series of experiments.

The results obtained when a single wire was enclosed within the large chamber are shown in fig. 5, in which the values of the heating current are plotted as abscissæ against the corresponding resistance of the wire as ordinates. The curves A_1 and A_2 refer to the cases where the single wire was surrounded by air at pressures equal to 760 mm.

* See Barratt, Proc. Phys. Soc. vol. xxviii. part 1, p. 10 (1915).

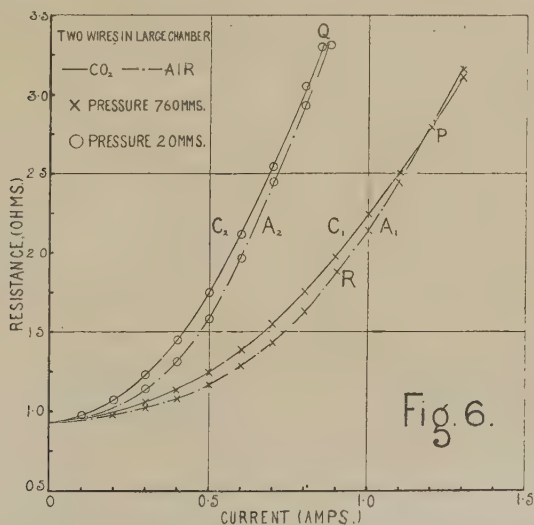
and 20 mm. respectively. The curves C_1 and C_2 have similar reference to the case where the chamber was filled with carbon dioxide. It is seen from curves A_1 and C_1 that for values of the heating current such that the temperature of the wire is below that corresponding to P—about 606°C —the wire when surrounded by carbon dioxide is hotter than is the case when air surrounds the wire. This would be anticipated from the greater value of the thermal conductivity of air compared with that of carbon dioxide. For values of the heating current greater than 1.14 amp. corresponding to P the wire is hotter when surrounded by air. At these temperatures the calculated value of the



thermal conductivity of air is still greater than that of carbon dioxide (see Table on page 952), but the ratio approaches more nearly to equality as the temperature is raised. It is clear, therefore, that the difference in temperature of the wire in the two media is conditioned principally by differences in the respective convection losses at high temperatures, whereas at low temperatures such difference is conditioned principally by differences of conduction losses. At 2 mm. pressure the corresponding curves A_2 and C_2 intersect at Q corresponding very nearly to the same temperature as that represented by P.

The effect of the introduction of a second wire parallel to the first, separated by a distance of 1.5 mm., and heated by

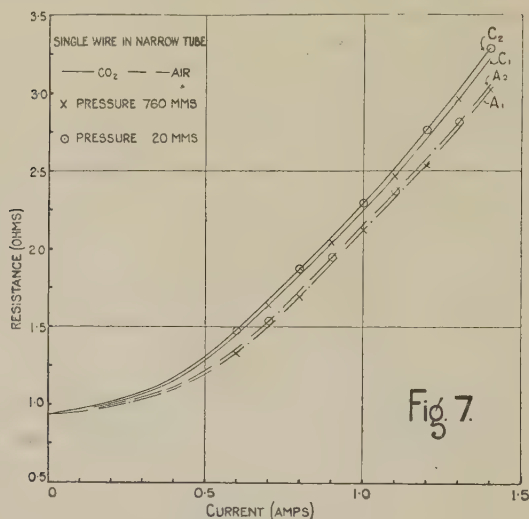
the same current, as in the inclinometer, is seen in fig. 6. The notation of the curves is the same as in fig. 5. The point of intersection of A_1 and C_1 in fig. 6 occurs at a higher temperature than is the case in fig. 5. This indicates that under conditions such that equal total dissipation of energy would occur from the wires in the two cases, the proportion of convection loss to the total loss from a wire would be less in the case of a wire constituting one of a pair disposed as described, than would be the case when one wire alone was heated in the chamber. Results obtained when the pressure in the chamber is reduced to 20 mm. (curves A_2 and C_2 , fig. 6), show that under these conditions differences in the



respective convection effects become still less relatively important, the curves not intersecting within the range of heating currents employed.

In the small chamber as shown in fig. 7, the difference of the temperature in the two cases when a single wire is surrounded by either air or carbon dioxide as shown by the curves A_1 and C_1 , or A_2 and C_2 , is conditioned under all conditions principally by conduction effects. As seen from a comparison of the curves A_1 and A_2 , or C_1 and C_2 , convection losses are practically entirely absent, and the temperature of the wire in one or other gas when heated by a constant current is only very little higher when the pressure is 20 mm. than when the pressure is 760 mm. of mercury.

The curves A_1 and C_1 in fig. 7 are of some interest in another connexion. The fact that a fine platinum wire carrying a constant current becomes heated to different temperatures when the gaseous medium surrounding the wire is altered, forms the basis of Shakespear's katharometer* originally employed for the determination of the degree of purity of hydrogen. Recently the device has found industrial application for determining and recording the percentage of carbon dioxide in flue and other gases†. A Wheatstone bridge device is employed, a pair of arms being constituted of two fine heated platinum wires contained



within chambers filled respectively with the gas to be examined, and a gas of standard composition, the chambers being small so that convection effects are negligible. Carbon dioxide present in flue gases is diluted principally with nitrogen and oxygen, and the gases may be sampled at a temperature of 300°C ., or higher, and subsequently cooled to atmospheric temperature. Now it is evident from fig. 7 that a change from 0 to 100 per cent. in the carbon dioxide content of the flue gas would alter the resistance of the wire immersed in the gas by about 9 per cent. at the most.

* See Proc. Roy. Soc. vol. xcvii. p. 273 (1920).

† See Daynes, Proc. Phys. Soc. vol. xxviii. p. 165 (1921).

Efficient control of combustion processes requires the carbon dioxide content of flue gases to be maintained constant, certainly to within 1 per cent., which would correspond to a change of approximately 0.09 per cent. in the resistance of the wire immersed in the sampled gas. Such a difference of resistance of the wires in the respective chambers would arise owing to a difference of about 0.25° C. in the temperatures of the gases in the respective chambers. Equality or constancy of the difference of temperatures of the gases in the two chambers to within about 0.03° C. is therefore necessary, if the indications of the instrument are to be comparable in accuracy with that easily obtainable (0.1 per cent.) with various forms of gas analysis apparatus in which the carbon dioxide content of the gas is determined by observation of the gas volume before and after the absorption of that constituent.

The author desires to express to Dr. Charles Carpenter C.B.E., his thanks for the provision of facilities for carrying out the work detailed herein.

709 Old Kent Road, S.E. 15.
29 January, 1923.

XCVII. Cathodo-Luminescence and its Relation to States of Molecular Aggregation. By J. EWLES, Assistant Lecturer in Physics, Leeds University.*

THE term luminescence seems to have been first introduced by Wiedemann to denote all the cases of re-emission of absorbed energy as light. The absorbed energy may be derived from light (including ultra-violet and infra-red), X-rays, cathode rays, or the radiations from radium.

Although the phenomenon has been the subject of careful investigations for a number of years and a considerable amount of experimental evidence has been obtained, there has yet appeared no satisfactory general explanation of all the facts. Indeed, the evidence on the surface appears to be so complicated and diverse that a statement of the general conclusions is impossible without a certain degree of selection.

* Communicated by Prof. R. Whiddington, M.A., D.Sc.

The following facts, however, emerge as being important :—

I. Nature of spectra.

- (a) All luminescent spectra, however excited, are arranged in bands showing equal frequency differences*.
- (b) An intimate relation exists between the luminescent spectra of a body and the absorption spectra. It seems probable that under similar conditions the one is the complement of the other †.

II. The effect of temperature is very variable.

Dewar ‡ found that many substances which luminesce at ordinary temperatures do not do so at the temperature of liquid air, and *vice versa*.

At low temperatures the broad bands break up into narrower bands §. There is an upper limit of temperature beyond which luminescence || ceases.

III. The effect of impurities is very marked.

- (a) Pure substances do not luminesce ¶.
- (b) Luminescence results from admixture of a small amount of impurity called by Bruninghaus the Phosphorogene**.
- (c) Different impurities affect the colour of the luminescence differently by affecting the relative intensity and distribution of the bands ††.
- (d) There is always an optimum of luminescence corresponding to a certain small and fixed percentage of impurity ‡‡.

* Wood, 'Physical Optics.' Nichols and Merritt, *Phys. Rev.* 1912. Howes and Wilber, *ibid.* 1917. Nichols and Howes, 1916 & 1918, *ibid.* Mrs. F. G. Wick, *ibid.* 1918. Nichols and Wilber, *ibid.* 1920.

† H. and J. Becquerel & K. Onnes, *Konink. Akad. Wetensch. Amsterdam*, 1909. J. Becquerel, *C. R.* 1910.

‡ Dewar, *Proc. Roy. Soc.* xiv. (1895).

§ J. Becquerel, *C. R.* 1907. H. Becquerel, *C. R.* 1907.

|| Lenard and Klatt, *Ann. der Phys.* xv. (1904). Nichols and Wilber, *Phys. Rev.* 1921.

¶ Urbain and Bruninghaus, *Ann. Chem. et Phys.* 1909. Mourello, *C. R.* cxxiv. 22, 1237. Nichols, Howes, and Wilber, *Phys. Rev.* 1918. Nichols, Howes, and Wick, *ibid.* 1919. Grüne, *Ber. Deutsch. Chem. Gesell.* 1904.

** *Loc. cit.*

†† Mourello, *C. R.* cxxvi., and Becquerel, *C. R.* cvii.

‡‡ Lenard and Klatt, *Wied. Ann.* 1889.

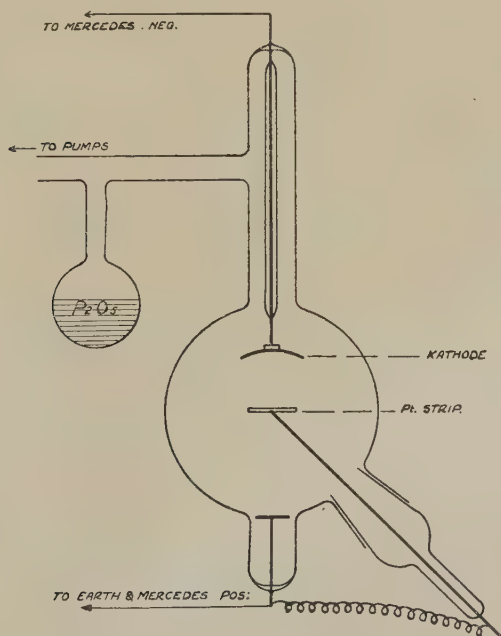
IV. The state of aggregation of the substance is a determining factor in the nature or very existence of luminescence and equally in the character of absorption bands*.

This is discussed at length later in this paper.

V. With increasing frequency of the exciting radiation, *i. e.* greater energy, the luminescent spectra extend further into the violet.

Experiments were begun with the object of determining whether the luminescence excited by cathode rays appears only when the rays acquire a minimum speed, *i. e.* whether a definite quantum of energy is required to excite the luminescence. It was thought that such an investigation might lead to some indication as to the nature of the processes giving rise to luminescence.

Fig. 1.



Some twenty metallic oxides and several other substances were examined. The substances were deposited in a thin layer on a strip of platinum mounted in a vacuum flask at the focus of a concave cathode (fig. 1). The tube was excited by a

* Wood, 'Physical Optics.' Hodgson, Phys. Rev. 1918. Nichols and Wilber, Phys. Rev. 1917.

Mercedes electrostatic machine, and the voltage applied controlled by the pressure of the residual gas and measured by a Kelvin and White electrostatic voltmeter. It was found that the cathodo-luminescence did not appear until the potential applied to the tube reached a certain critical value.

That is, for each substance, the cathode rays must possess a minimum amount of energy before luminescence is excited.

Details of the results are shown in Table I.

TABLE I.

Substance.	Colour of Luminescence.		Minimum voltage for excitation.
MoO	Blue	faint.	3400
ZrO	Mauve	strong.	1200
Fe ₂ O ₃	{ Greenish-yellow }	faint.	{ 1500 (see also Table II.). }
CaO	Yellow	strong.	1050
CaS	Yellow	strong.	950
BaO (impure)	Yellow	strong.	2150
BaO (AR)	Yellow	strong.	700
Cr ₂ O ₃	Blue	faint.	3800
WO ₃	Blue	faint.	5200
BiO ₃	Orange	faint.	1900
MnO ₂ (pyrolusite) ..	GY → RY	faint.	3400
SrO	Blue	faint.	1350
CuO	Violet	faint.	1100
Cu ₂ O ..	Violet	faint.	1400
Sb ₂ O ₃	Whitish	faint.	1700
PbO	Whitish	faint.	1900
SnO	Whitish	{ moderately strong. }	1425
SiO ₂	Blue	brilliant.	750
Al ₂ O ₃	Blue and pink.		{ 580-650 (according to sample). }
MgO } ZnO }	See Table II.		

In each case the potential corresponding to first appearance with increasing voltage and to disappearance with decreasing voltage was observed many times.

One is well aware that the possibility of determining the exact point of appearance or disappearance is limited by the sensitiveness of the eye, and the minimum voltages obtained must in all cases be too high.

In many cases, however, the luminescence came in so sharply as to leave no doubt as to the existence of a very definite minimum. More exact measurements are in progress which do not depend on the sensitiveness of the eye.

Nichols and Howes (Phys. Rev. 1921) have plotted curves, showing intensity of luminescence against voltage, which show the existence of a minimum voltage for luminescence. They do not appear to have taken into account the variation of the cathode ray current with voltage, so that the actual values obtained are hardly reliable.

Examination of the results shown in Table II. brings out the following points :—

(1) For each substance showing cathodo-luminescence there is a critical speed of rays required to excite it which is characteristic of the particular substance.

(2) A comparison of the minimum energy required in the case of similar oxides shows that no simple relation exists between the energy change and the atomic numbers of the metals. This suggests that the transformation is not atomic.

(3) Nor does there appear to be any simple relation between the minimum energy and the heat of dissociation or formation such as would be expected on the suggestion put forward by Baly and others that the change involved is a chemical one.

It was found, indeed, that even with the same chemical substance, all precautions being taken against the entry of new impurities, the method of preparation has a marked effect on the critical energy, colour and intensity of the luminescence. Each sample shows some difference, often very marked, in the colour, intensity, and critical speed for excitation.

These results show how the state of aggregation of a substance affects its luminescence. This is in agreement with the observations of many previous workers on cathodo- and other types of luminescence.

Levy (Röntgen Soc. Journ., Jan. 1916) showed that the colour and intensity of the fluorescence of barium platino-cyanide is different in the two crystalline states and in the amorphous state.

M. B. Hodgson (Phys. Rev., Dec. 1918) showed that the X-ray luminescence of calcium tungstate depends on its crystal structure.

Baly and Tryhorn (Phil. Mag. xxxi.) find that the position and depth of the absorption bands of pyridine and salicylaldehyde vary with the concentration.

Waentig (*Zeitschr. Phys. Chem.*) found that the phosphorescent alkaline-earth sulphides passed when rubbed into coloured non-luminous powders, which change is accompanied by a decrease of volume and an absorption of energy.

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TABLE II.

Zinc oxide, from pure zinc *.

Method of Preparation.	Colour of Luminescence.	Minimum voltage for excitation.
1. Sublimed from zinc arc.	Green.	650
2. Zinc hydroxide pptd. from cold solution and ignited	Bluish-white.	850
3. Sample from (2) heated for one hour at 1200° C.	Yellowish-green.	350
4. Zinc hydroxide pptd. from hot solution and ignited.....	Red and green together.	400
5. Zinc ignited in air	Green.	580
6. Zinc nitrate ignited.....	Orange.	650
7. Sample from (6) heated at one spot to incandescence	Heated part green. Unheated part orange. }	550
8. Zinc carbonate ignited...	Green.	725
9. Sample from (8) heated to incandescence	Green.	400

* Analytical reagent manufactured by British Drug Houses Ltd.

Magnesium oxide, from magnesium AR.

1. Smoke from burning Mg deposited on a hot platinum strip	Rose and sky-blue.	650
2. Smoke from burning Mg deposited on a cold platinum strip	Rose and sky-blue.	1200
3. Mg(OH) pptd. and ignited	Sky-blue.	1200
4. Mg(NO ₃) ₂ ignited	Faint blue.	1700

Natural crystalline Fe₂O₃.

1. Small crystals about 1 mm. dimensions	Faint red; blue at higher voltages. }	4000
2. Crushed to powder in an agate mortar	Whitish-blue; phosphorescent for some minutes. }	1000
3. Crushed to very fine powder and then "rolled" in an agate mortar.....	No fluorescence.	—

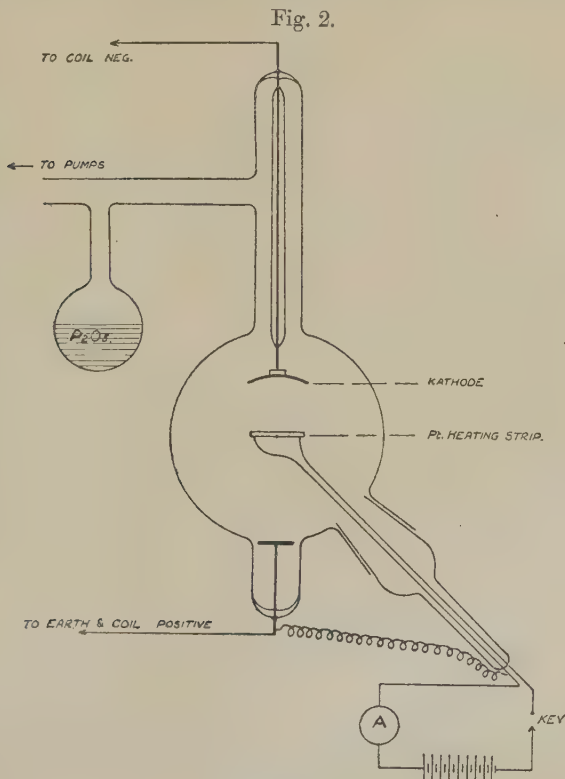
Silicon.

1. Amorphous	Whitish-yellow.	1600
2. Crystalline	Red.	2400

Imof (*Phys. Zeitschr.* 1917) finds a minimum-sized crystal necessary for tribo-luminescence.

Lenard and Klatt showed that the alkaline-earth sulphides lose their luminescent properties if subjected to high pressures. See also Beilby ('Aggregation and Flow of Solids'), Sect. xi.; S. E. Shepherd (*Illum. Eng. Lond.*, June 1917); T. R. Merton (*Chem. Soc. Journ.*, Jan. 1914); Farnau (*Le Radium*, June 1914).

Following up the train of thought suggested by these results, substances were taken which were known or could be shown to undergo a change of molecular aggregation if heated beyond a certain temperature. For example, quartzite exists in two forms, α and β , differing in density and refractive index, a reversible change from the α to the β form taking place at 575°C . Such substances were examined with a view to determining whether any change takes place in the cathodo-luminescence at the temperature



of transformation. The substances were deposited in a thin layer in the middle of a strip of platinum which could be raised to any desired temperature by the passage of a steady current. The magnitude of the current, measured by a Cambridge and Paul ammeter, gave the temperature, the strip having been previously calibrated by determining the current required to melt various salts of known melting-points. The calibration curve was checked at the higher temperatures by a Cambridge optical pyrometer.

The platinum strip acted as the anode (see fig. 2) so that the rays from the cathode could be fired at the substance deposited on it. The source of high potential in these experiments was an induction-coil which could be switched on and off rapidly so as to avoid, as far as possible, heating the substance by the rays.

In order to test whether the momentary flash of cathode rays appreciably raised the temperature of the substance, the intensity of the rays was varied by altering the residual gas-pressure and by varying the current in the primary of the coil. No appreciable variation of the temperature of disappearance could be detected.

In those cases where the transformation temperature was not already known, this was determined by the Roberts-Austen differential heating or cooling curve method. In this method the substance under test is heated in an electric furnace by the side of a standard substance which is known to undergo no transformation. Thermocouples of platinum and an alloy of 90 per cent. platinum and 10 per cent. rhodium are imbedded in each and connected in opposition to a sensitive galvanometer. The temperature of the sample is obtained by a third thermocouple. Any molecular transformation absorbs or generates heat, so that the temperature of the test material when the transformation takes place lags behind or advances on that of the standard substance, and this difference in the temperatures is at once indicated by a deflexion of the differential galvanometer. For the suggestion of this method and help in carrying it out, I owe thanks to H. S. Houldsworth, of the Fuel Department of Leeds University.

Experiments on fourteen different substances gave the remarkable result that above the temperature of transformation the cathodo-luminescence disappears.

The results are summarized in Table III.

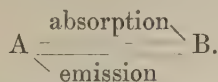
The remarkably close agreement shown in the above table between the transformation temperature and the temperature of disappearance of the luminescence indicates an intimate relation between the processes involved in the molecular rearrangement and the emission of luminescence. The fact that the sample of alumina which showed no transformation also showed no luminescence is highly significant.

The evidence seems sufficient to warrant the hypothesis that luminescence is a manifestation of the energy change involved when a substance changes from one state of molecular aggregation to another. Any theory of luminescence must take into account the intimate relation between

TABLE III.

Substance.	Nature of Transformation.	Temp. of Transfn.	Disappearance of Fluorescence.
Zinc oxide	{ Sudden change of density and resistance. }	700°	700°
Magnesium oxide	Slow change to periclase.	{ 900° (begins). }	930°
Zirconium oxide	Slow change of density.	700°	730°
Alumina (by ignition)..	Change of density.	1060°	1060°
NaOH.....	299°·6	293°
KOH	248°	242°
Wollastonite (CaSiO ₃).	Pseudo-wollastonite.	1197-1232° (according to the rate of heating).	1240°
Calcium orthosilicate (2CaO)SiO ₂	{ Large volume change with powdering. }	675°	680°
Cyanite	Change to sillimanite.	1300°	1330°
Quartzite.....	{ Change of μ and 0·5% volume expansion. }	575°	575°
K ₂ SO ₄	580-599°	600°
LiSO ₄	575°	570°
CaSO ₄	666°	680°
Alumina (pptn. from Al ₂ (SO ₄) ₃ by NH ₄ OH and ignition	{ No transformation occurs. }	1065°	No fluorescence.

luminescent and absorption spectra pointed out earlier in this paper. Indeed, it seems justifiable to make the assumption, as most recent writers on the subject have done, that the two processes correspond to different aspects of the same reversible change, the system absorbing in one direction and emitting luminescence in the other. Thus :—



The fundamental difference in the general formula expressing the distribution of frequency in band spectra, $=A+Bm+Cm^2$, involving only positive powers of m , and the general formula for line spectra, involving negative powers of m , may be taken to indicate a corresponding difference in the structure of the systems whose changes of energy give rise to the two different kinds of spectra.

The results of the experiments described above suggest that the system in the case of luminescent and absorption spectra is an aggregate of molecules. The extremely important part played by impurities in the nature and even existence of luminescence mentioned earlier helps to form an

idea of the possible structure of the radiating system. Sir J. J. Thomson (Phil. Mag., May 1914) shows that certain special types of molecules containing oppositely charged atoms may act as electrical doublets, and by virtue of their strong electrostatic fields possess the power of condensing a large number of other molecules round them. This action, he maintains, will involve molecular rotations when the system is being formed or rearranged. We might imagine, then, the bipolar nucleus of impurity, with its cluster of surrounding molecules, as playing the same part in the emission or absorption of band spectra as the Bohr atom, with its positive nucleus and surrounding electrons, plays in the production of line spectra.

The changes of energy of the electrons in the atom giving rise to line spectra are here replaced by changes of the molecular rotational and oscillational energy, as the aggregate is formed or rearranged, giving rise to the emission or absorption of band spectra. This view gives a physical aspect to the Schwartzschild development of the band-spectra formula. This author has shown that the general band-spectrum formula can be arrived at by applying quantum considerations to the changes of rotational and oscillation energy of molecular doublets.

The theory of luminescence here advanced seems to offer a reasonable explanation of all the experimental data. It explains why, as Baly (Phys. Rev. 1921) pointed out, the frequencies in absorption spectra are multiples of a common molecular frequency characteristic of the substance.

Lenard and Klatt (*Ann. der Physik*, 1904) found that in certain cases a flux was necessary for luminescence. The action of the flux may be explained as facilitating molecular rearrangement.

In phosphorescence we may suppose that the stimulus brings about the reversible change in the direction involving absorption, the return to the former state with the emission of energy as phosphorescence going on for some time after the stimulus is removed.

The phenomenon of thermo-luminescence observed by Wiedemann, namely, that certain substances did not show luminescence while being stimulated but after removal of the stimulus and subsequent heating gave out luminescence, is accounted for by supposing that the stimulus brings about molecular rearrangement into a metastable condition and that subsequent heating is necessary to reverse the change.

The very variable effect of temperature follows directly from the theory. Temperature determines the state of

aggregation, and the fact that a substance may not luminesce above or below a certain temperature indicates that any change that can occur will be in a direction involving absorption.

Taking the minimum energy required to excite cathodo-luminescence, as determined in the above experiments, to represent the quantum of energy required to transform the molecular aggregate, and assuming equipartition of this energy among the constituent molecules of the aggregate, it should be possible from a knowledge of this energy and the molecular heat of transformation to determine the number of molecules composing the aggregate. For example:—

The critical potential for zinc oxide varies with the sample, as indicated above, from 350 to 850 volts. The energy per electron corresponding to this is 5.565×10^{-10} erg and 15.421×10^{-10} erg respectively.

The heat of transformation of zinc oxide is 4.41 kg.-cals. per gram-molecule, *i. e.*

$$\frac{4.41 \times 10^3 \times 4.2 \times 10^7}{60.6 \times 10^{22}} = 3.06 \times 10^{-13} \text{ erg per molecule,}$$

which gives a molecular aggregate of 1818 in the lowest case and 4271 in the highest. The writer is well aware, for the reasons stated earlier, of the very approximate nature of these numbers. Experiments are in preparation, however, for a more accurate determination of the minimum cathodic energy and a parallel determination of the energy of transformation, from which it is hoped to obtain fairly reliable results as to the number of molecules in an aggregate. It is hoped also to obtain an estimate of a minimum possible number of molecules which can form a crystal, in various cases.

Summary.

I. A generalized survey of the chief results obtained by previous workers on luminescence.

II. Experiments with cathode rays on a number of substances indicate that each substance showing cathodo-luminescence requires a minimum speed of cathode rays to excite the luminescence. This speed appears to be characteristic of the substance, but depends also on the state of aggregation.

III. The temperature at which cathodo-luminescence disappears coincides, in the case of all substances examined,

with the temperature at which a molecular transformation takes place.

IV. A general theory of luminescence suggested by these results is put forward.

In conclusion, I wish to express my very great indebtedness to Professor R. Whiddington, who suggested the original problem, for his continual advice and encouragement throughout.

Physics Department,
The University, Leeds.

XCVIII. *Some Observations on the Ignition of Combustible Gases by Electric Sparks.* By J. D. MORGAN, M.Sc.*

IT has been shown by calculations that the amount of heat energy that must be imparted to cause ignition of a combustible gas mixture can vary greatly with the conditions under which the heat is supplied (Taylor Jones, Morgan, & Wheeler, *Phil. Mag.* vol. xliii. Feb. 1922). In making the calculations, it was assumed that ignition is a thermal process involving the raising of a certain volume of the gas to a certain temperature, and that the heat is communicated from the source to the gas by conduction. The heat energy required in the source to produce ignition is least when the heat is imparted instantaneously. When the rate of heat supply is less a greater quantity of heat must be given to the gas before ignition can occur. It was also shown that variations in the shape or linear dimensions of the heat source would result in variations of the heating effect.

The sparks used for ignition of combustible gases are of two kinds (capacity and inductance sparks) which differ notably in temperature and duration. The spark produced by a single discharge from an electrostatic condenser across a gap between stationary electrodes has, judged by its luminosity, a very high temperature, and is of extremely short duration; whilst that produced during separation of a pair of contacts in an inductive circuit has a lower temperature and is usually of relatively long duration.

The results of previous experimental work on spark

* Communicated by Prof. E. Taylor Jones.

ignition are characterized by remarkable diversity. Nevertheless, there emerges the general conclusion that to ignite a given gas mixture a larger amount of heat must be imparted by an inductance spark than by a capacity spark, and the differences observed are broadly such as are consistent with the hypothesis that ignition is a thermal process.

At first sight it would appear to be easy to submit the theoretical deductions above mentioned to quantitative tests. Closer examination shows, however, that serious and possibly insuperable difficulties lie in the way, and it becomes doubtful whether additional experiments can do more than confirm the general agreement that already exists between the thermal hypothesis and experimental results. Further, it would appear that development of the thermal hypothesis is more likely to depend on an accumulation of indirect evidence than on direct demonstration.

It has been shown by Patterson and Campbell (*Proc. Phys. Soc. of London*, vol. xxxi. pt. iv. June 15th, 1919) that the energy required for ignition of a given gas mixture by a capacity spark (instantaneous heat source) may be a widely variable quantity. In expressing their results they correlated the spark energy and the sparking voltage of the gap at which the igniting sparks were produced. No explanation of the results was suggested.

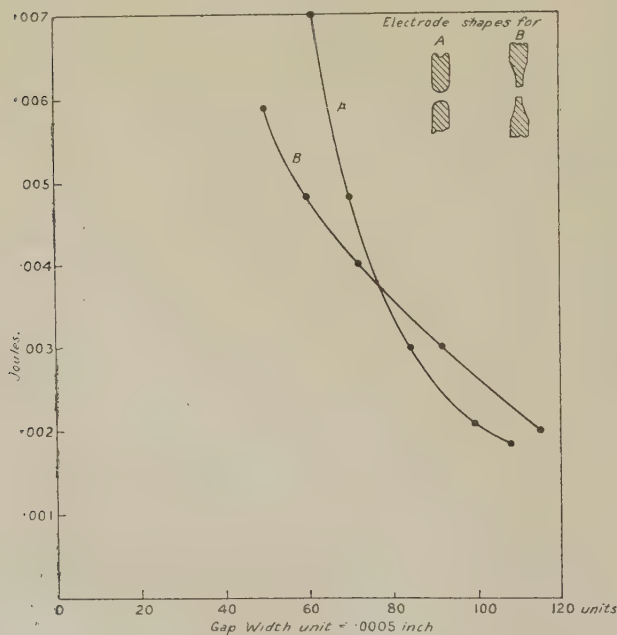
The fact observed by Patterson and Campbell is one of considerable practical importance in connexion with the ignition of gases in internal combustion-engines. It appeared to the writer to be one of theoretical importance also. He decided therefore to repeat and extend their experiments with a view to comparing the results with the thermal hypothesis of ignition.

The curve A, fig. 1, was obtained from experiments on a mixture of methane and air (about 8.8 per cent. methane). In the same diagram is shown the shape of the spark-gap electrodes. The sparks were produced by discharge of a variable condenser across a gap of variable width. Charging of the condenser was effected by means of an induction-coil acting through a thermionic valve. To find each point on the curve the condenser was adjusted to a particular value and the gap width was increased until ignition occurred. In expressing the results, the energy in the system prior to the occurrence of the spark is taken as a measure of spark-energy, and this is correlated with spark-gap width.

The conditions of the experiments though apparently simple are really very complex. At least three important

variables are involved, and each of these affects the results in a probably indeterminate manner. These variables are (1) the spark-length, (2) the configuration of the gas region immediately adjacent to the spark, and (3) the area of cooling surface presented by the electrodes to the incipient flame. Probably the effect of variation of spark-length is negligible in comparison with the other two, and attention has therefore been confined to them. It does not appear to be possible to separate the effects of these two without incurring other serious difficulties. That a change in the

Fig. 1.

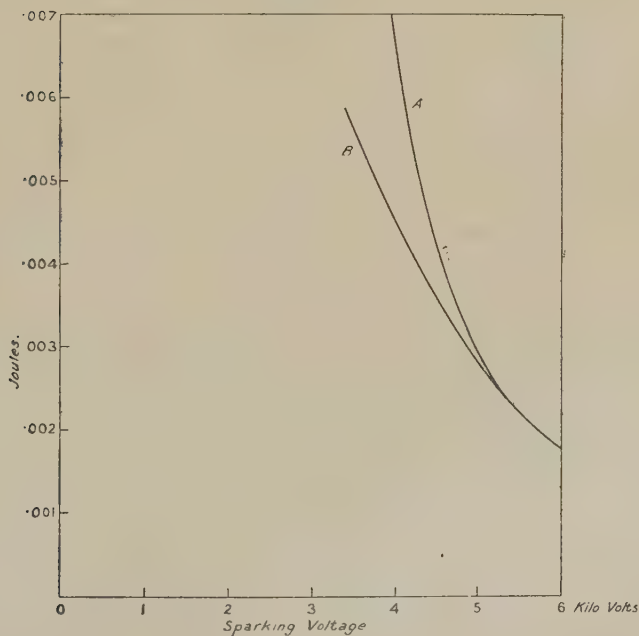


configuration of the gas region adjacent to the spark has an important effect, is evident from curve B. To obtain this curve the shape of the electrodes was altered as shown in the diagram, but the curvature at the sparking position was kept the same as before in order to minimize as much as possible any consequent variation of the sparking voltage. It might be said that the alteration of shape also resulted in an important reduction of cooling effect by the electrodes, but there is reason to believe that the difference between the curves A and B is less due to cooling than to increase in

the volume of gas immediately adjacent to the spark, though it must be admitted that variation in the cooling effect of the electrodes is involved in the results.

It will be noticed that the curves intersect. This is due to the fact that at the larger gap-widths the sparking voltages of the two gaps were not quite the same. When the spark energy is plotted against spark voltage, the two curves coincide at their lower ends as shown in fig. 2. Similar results were obtained from experiments on coal-gas and blast-furnace gas.

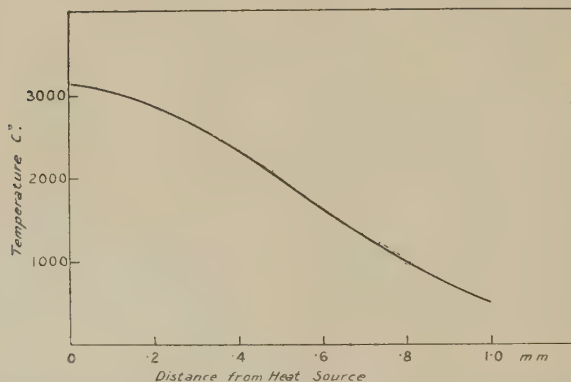
Fig. 2.



The problem to be considered is as to whether or not such results as those shown in figs. 1 and 2 are consistent with the hypothesis that ignition depends on raising a certain volume of the gas to a temperature not less than the ignition temperature. The calculations recorded in the paper previously referred to afford a basis for a definite affirmative answer. It was shown that the temperature wave, resulting from the instantaneous discharge at a point in the gas of a certain quantity of heat, assumed, after an interval of time,

the form shown in fig. 3, the volume of gas in which no part was at a temperature below 700° being then a maximum. To correlate the experimental results with the curve in fig. 3, two assumptions will be made. Wheeler has shown that the initial form of a flame resulting from the ignition of a gas by a spark is approximately of the same shape as would result from rotating a V about an axis through its ends, the axis being also the axis of the spark. This shape suggests

Fig. 3.



that the cooling effect of the electrodes is such that the most effective portion of the spark is at or near the centre of its length. The first assumption is, therefore, that the heating effect produced by a short linear spark will not be greatly different from that of a point. The second assumption (made to simplify the problem) is, that the gap electrodes are formed with flat ends, and the thermometric conductivity of the electrodes is the same as that of the gas

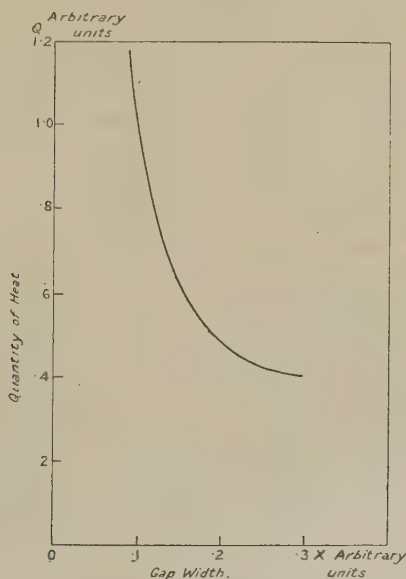
Fig. 4.



in which the spark passes. The diagrams in fig. 4 show two positions of the gap electrodes, and the circular lines indicate the boundaries of two equal volumes of gas contained

between the electrodes. It will be evident that to raise the boundary of the volume of gas shown by *b* to the same temperature (say, $700^{\circ}\text{C}.$) as the boundary of the gas volume shown by *a*, will require a larger quantity of heat in the source. Indicating the gap-width by x and the quantity of heat required in the source by Q , the relationship between Q and x has been calculated from the curve shown in fig. 3. The result is shown in fig. 5. It will be seen that the general form of the curve is the same as that of the experimental curves A shown in figs. 1 and 2.

Fig. 5.



Though no quantitative comparison can be made between the hypothetical and actual curves, the agreement of general form affords important evidence in support of the thermal hypothesis. The differences which must be made in the hypothetical curve to compensate for the assumptions made in obtaining the curve are not such as will cause any alteration in the character of the curve.

Incidentally, the experiments serve to illustrate the important fact that the heat required to cause ignition of a given gas mixture is a quantity that can vary greatly with the experimental conditions, even when sparks of the same type are used. The results obtained by different investigators

can never be comparable unless carried out with identical apparatus. At one time the diversity of results was the cause of much perplexity. It has since become increasingly apparent that this perplexity was due mainly to a misconception of what was implied by the supposition that ignition is a thermal process.

Experimental.—When capacity or condenser sparks are used in ignition experiments it is usual to calculate the spark energy from the expression $\frac{1}{2} CV^2$, where C is the capacity across the gap and V the sparking voltage of the gap. Knowing that the results of this procedure could be misleading, the matter was subjected to a close examination, and some interesting effects were observed. At first it was the intention to use a number of small glass condensers of about equal capacity, and arrange for one or more to be connected in parallel with the gap in the explosion apparatus. These were calibrated by charging to a known potential and discharging through a ballistic galvanometer. Then a small spark-gap was arranged in series with the galvanometer circuit, and the calibration experiment was repeated. As was anticipated, the discharge through the galvanometer was less than when the gap was not present. It was noticed, however, that the ratio of the two discharges was not a very regular quantity and was not the same for all the condensers, and the calibration graph correlating quantity of discharge across the gap and the total capacity of the condensers in operation showed well-marked "steps." If these condensers had been used in the explosion experiments and the spark energy had been expressed, as usual, by $\frac{1}{2} CV^2$, the true results would have been masked by irregularities due to the behaviour of the condensers. Condensers with other solid dielectrics were tried, and in all cases similar effects were observed. Finally, a variable air-condenser was constructed, and with this the irregularities disappeared. The ratio of the discharges under the two conditions above mentioned was perfectly regular and consistent. Its value for one gap setting was .87. In figs. 1 and 2 the energy was calculated from the known values of C and V , and as the results were only required for comparative purposes, the correction for "gap effect" was not applied. The experience gained in this investigation showed that with condensers having solid dielectrics serious discrepancies could arise, and that these could be avoided successfully by the use of air-condensers.

As already stated, the condensers were charged at a relatively slow rate in the explosion experiments, from an induction-coil acting through a thermionic valve. By

this means irregularities in the sparking voltage due to "impulsive" effects* were avoided. Nevertheless, serious irregularities in the sparking voltage of the gap were observed, and these for a time caused much trouble. When the gap was exposed to the open air of the laboratory it behaved with great regularity and consistency. But when put into operation within the explosion apparatus no two discharges occurred across the same gap-width at the same voltage, and often the sparking voltage required to produce a spark was double the normal sparking voltage of the gap. Different metals were tried in the gap-electrodes, namely, platinum, steel, nickel, and brass, and all gave similar results. The procedure followed in each ignition experiment was to evacuate the explosion chamber and let in a charge of previously prepared gas mixture from a holder, the gas on its way from the holder being caused to pass through a drying agent. Ignition of the charge was effected at atmospheric pressure. As causes of the irregularities in the sparking voltage, electrode surface condition and deficient ionization of the gas were suspected. The experiments made to ascertain the cause did not, however, lead to any definite results. The balance of evidence appeared to indicate that the trouble was due to deficient ionization, but the discovery of a simple remedy made it unnecessary to examine the matter further. It was found that by reducing the gap to a relatively small amount after each introduction of a fresh charge, and causing one or two small sparks to pass (insufficient to have any appreciable effect on the gas) the irregularity could be almost entirely removed. With experience in the use of the apparatus it became easy to detect "over-voltages," especially when an ammeter was arranged in the primary circuit of the induction-coil and the primary current adjusted so that the secondary discharges were only sufficient to raise the condensers to the normal sparking voltage of the gap.

The unit of gap measurement adopted was $\cdot 0005$ of an inch, and in the methane-air experiments it became possible to obtain a high degree of accuracy and consistency. With a given capacity in the system, the gap settings necessary to cause ignition in a dozen successive trials would not vary by more than one unit of gap-width. All the points on the curves shown in fig. 1 were obtained under these conditions. Using coal-gas and blast-furnace gas, the results were less regular and the gap settings necessary to cause ignition could not be ascertained to less than $\cdot 001$ of an inch.

* "Impulsive Sparking Voltages," *Phil. Mag.* vol. xli. March 1921.

XCIX. *The Theory of the Trevelyan Rocker.*
 By E. G. RICHARDSON, M.Sc. (*East London College*) *.

WHEN Arthur Trevelyan, Esq. (as he is described in the Transactions of the Royal Society, 1831), accidentally discovered † that an iron fork laid on a block of lead gave rise to musical sounds, he set to work to devise a model which should best exhibit the effect, and produced the well-known prismatic block of copper having a groove in its under surface so that it would rock on the ridges, the other point of support being a knob at the end of a thin round handle. Sir John Leslie suggested a theory of the action, which was accepted by Trevelyan and remained unchallenged, save by Forbes, until recently. Trevelyan found it necessary to have the ridges very smooth and clean, but the lead was best roughened. Heat being communicated to the lead by the copper, the rugosities of its surface were supposed to expand, to push up each ridge in turn, and then to contract as the heat diffused through the lead, the rocking being due to inequality of inertia of the portions of the rocker on opposite sides of the ridge, or to a difference in condition of the lead on either side of the line of contact with the ridge, causing a lateral movement. Faraday ‡, as a result of experiments with various pairs of metals, went further and said that the success of the experiment depended on the difference of conductivity of the two metals; the hot one must readily transfer its heat to the cold one, but the heat must not be able to diffuse rapidly into the latter, but remain near the point of contact causing local expansion; it was immaterial which one formed the rocker, cold lead would vibrate on a hot copper block.

However, Forbes § was unable to substantiate Faraday's conclusions, and advanced a new theory that the phenomenon showed evidence of a repulsion taking place when heat is transferred from a body of high conductivity to one of low. Seebeck || and Tyndall ¶ put Forbes' argument against Faraday's hypothesis thus: (1) the greater the expansion

* Communicated by Prof. C. H. Lees, F.R.S.

† A German workman had discovered it independently some years before (*vide* Gilbert, Pogg. *Ann.* xxii. p. 323, 1806).

‡ Journ. Roy. Inst. 1831.

§ Trans. Roy. Soc. 1833.

|| Pogg. *Ann.* li. p. 1 (1840).

¶ Phil. Mag. vii. p. 223, and viii. p. 1 (1834).

of the block, the greater the effect, but (2) the greater the conductivity of the block, the greater the expansion; therefore (3) the greater the conductivity, the greater the effect (whereas lead, a bad conductor, exhibits the effect best). They pointed out, however, that the expansion in (1) is vertical, whereas that in (2) is *total*; so that Forbes' objection to the original theory is invalidated. Further, Tyndall set aside Forbes's own hypothesis, because he succeeded in making a substance vibrate on one of equal conductivity, *e. g.* copper on copper, provided that the metal beneath was reduced to the points of wires or the edges of thin laminæ, so that lateral conduction in the underlying metal was prevented.

In further support of the theory that the phenomenon was maintained by heat, Page* made a light rocker vibrate on two rails connected to the terminals of an electric battery, the heat being produced by the thermoelectric effects at the points of contact.

Finally, Davis† embellished this theory by a mathematical investigation, in which, by considering the rate of transfer of heat to the cold metal, he obtained the height to which the surface is raised by a given difference of temperature and period of rocking, and so calculated the difference of temperature necessary to produce vibrations at a given rate in a rectangular parallelepiped with two parallel ridges. He concluded from his analysis that a difference of 50° to 100° C. would be sufficient to cause the rocker to vibrate 225 times per second. This result is in fair agreement with the earlier experiments of Sondhauss‡, who found minimum differences of temperature from 30° to 80° C., the minimum increasing with the time of swing.

The subject then lay dormant for nearly 50 years. Quite recently Chuckerbutti§ has succeeded in obtaining some actual values for the amplitude, or height to which the ridge rises, and for the corresponding frequency of the vibration, by a mirror carried on a thin rod, rolling on the back of the rocker. By reflecting light from this mirror on to a moving photographic plate, the motion was exaggerated several thousand times, and some excellent photographs obtained. By measuring these the amplitude could be calculated; the

* Sill. Journ. p. 105, 1850.

† Phil. Mag. xlv. p. 296 (1873).

‡ Pogg. Ann. cxv. pp. 71 & 177 (1873).

§ Proc. Indian Assoc. Sci. vi. p. 143 (1921).

frequency was found by tuning a sonometer to unison with the note. Mr. Chuckerbutti thinks that the old theory is inadequate, and that when the rocker has settled down to a steady musical tone, "the *elastic* vibrations of the rocker and handle-bar play an important part, and eventually entirely displace any such simple rocking movement as may occur in the earlier stages of the experiment."

The work described below was undertaken with a view to an investigation of the relative merits of the two rival theories (referred to in this paper as the "gravity" and the "elastic" theory) more thorough than that of Mr. Chuckerbutti. He gives only 7 values of the frequency and corresponding amplitude, whereas by the method to be described some 350 were obtained.

Method of observing Amplitude and Frequency.

A block of lead with rounded top is screwed down to the bench. A small hole is bored through the rocker, through which a thick steel knitting-needle is thrust and held in position by a small screw, so that the needle lies horizontally about the centre of the rocker, when the latter rests with its two ridges across the lead block. The end of the needle or indicator is observed through a microscope, which can be quickly brought to bear on the indicator by adjusting a couple of wooden wedges placed between the bench on which it rests and the barrel of the microscope. The light by which the field of the microscope is illuminated comes from a little electric lamp placed behind the slits of a stroboscopic disk, driven by an electric motor. When the disk is rotating, therefore, the illumination is intermittent, and its period may be made to coincide with that of the rocker by finding the *fastest* speed of the motor which makes the end of the needle appear stationary in the microscope. This speed was measured by a stroboscopic vibrator in conjunction with the usual print of differently spaced circles of dots, pasted on the disk. By using a micrometer eyepiece, and setting the disk slightly out of step with the rocker, the amplitude at the end of the indicator could be readily observed as the needle appeared to move slowly up and down.

A third observation was made at the same time as the other two, *i. e.* that of the temperature of the rocker, by a method due to Sondhauss. A hole bored in the back is filled with mercury, into which the bulb of a 0° - 360° C.

thermometer, supported above, is placed, without touching the vibrating rocker.

By placing a glass micrometer scale on the object table of the microscope and focussing, it is found that 1 cm. on the eyepiece scale corresponds to an actual distance of $\cdot 016$ cm. in the object plane, and as the length of the indicator to the centre of the rocker is in each case 10 cm., this corresponds to an amplitude of $\cdot 0016$ ($2a$) at the ridge, where $2a$ is the distance between the ridges. The magnification is therefore from 1000 to 2000 times.

Fig. 1.

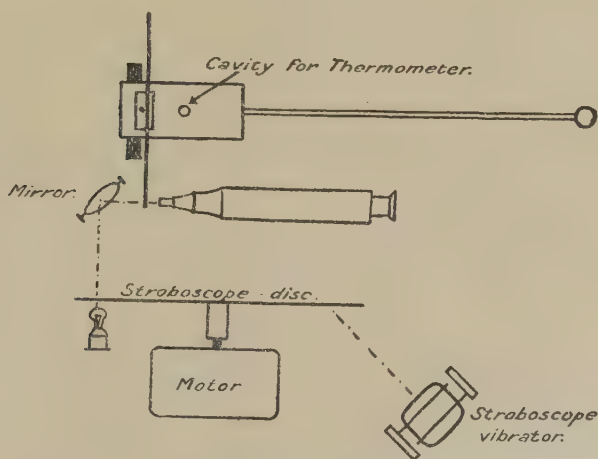


Diagram to show arrangement of apparatus (from above).

The first few tests with this apparatus gave amplitudes about 10 times those of Chuckerbutti, though the frequencies were of the same order. It was thought that perhaps the indicator exaggerated the vibrations, as it should do if their period were near its own. The needle was thereupon clamped at its centre, and its free vibrations (transverse) observed in the apparatus. Their frequency was found to be 168, which considerably exceeded any values obtained from the prismatic rockers. To make sure, two other tests were made. Firstly, another needle $\cdot 48$ cm. thick was passed through a parallel hole in the rocker so that its end and that of the original needle ($\cdot 19$ cm. thick)

could be simultaneously examined in the microscope. When the rocker was vibrating, the two rose and fell with the same amplitude, period, and phase (when examined by the method described above), showing that it was the vibrations of the rocker that were being observed, not the free vibrations of the needles, which, being of different thicknesses, would have exhibited different amplitudes when vibrating "freely" under resonance from the rocker*. Secondly, a galvanometer mirror was fixed on the back of the rocker so as to reflect light from a lamp on to a scale a metre above. When the rocker vibrated, the spot of light on the scale was drawn out into a band, whose length could be roughly determined†. The value of the amplitude calculated from this rather inaccurate measurement was of the same order as that obtained simultaneously from the needle under the microscope.

One reason why Mr. Chuckerbutti's values are low may be that he used a wooden block to press his rotating needle on to the rocker, and this probably acted as a restraint. A needle and wooden block having been lightly laid on the rocker (the other end of the wood being supported), it was found that the amplitude increased by $1\frac{1}{3}$ to 2 times when the needle and block were carefully lifted off the block by strings, and the "restraint" thus removed.

The Gravity Theory.

If M = mass of rocker, K its spin-radius, ϕ ang^r deviation from the vertical, $2a$ = distance between ridges, the equation of motion is

$$MK^2 \frac{d^2\phi}{dt^2} = -Mga.$$

An integration for $\frac{1}{4}$ -time-period gives

$$K^2\omega = agT/4$$

if R is the amplitude at a ridge, ω = angular velocity,

$$\frac{1}{2}\omega = \phi_{\max.}/\frac{1}{4}T \quad \text{or} \quad \phi_{\max.} = R/2a, \quad \text{and} \quad \omega = 4R/aT;$$

therefore

$$T^2 = \frac{16RK^2}{a^2g}.$$

* This test was also applied to the simple rockers described below, but at various frequencies between 50 and 200 no resonance was detected.

† A device first used qualitatively by Tyndall.

If n stand for the frequency, this equation may be written

$$n^2R = \frac{a^2g}{16K^2} *.$$

We see, then, that the gravity theory requires the amplitude and frequency to be connected by the formula $n^2R = \text{constant}$, whereas, if the vibrations are elastic, the frequency should be independent of the amplitude when the latter is small, but dependent on the length of the rocker and handle.

Results with Prismatic Rockers.

Two prisms were used, 12 cm. and 6 cm. long respectively, provided with two interchangeable handles, also of copper, 32 cm. and 24 cm. long, ending in brass knobs.

The observations are recorded in the following tables:—

$$2a = .5 \text{ cm.}$$

K^2 (for an isosceles triangle, height b , base c , about an axis perpendicular to plane through vertex) $= \frac{c^2}{24} + \frac{b^2}{2} = 3.98 \text{ cm.}^2$,

whence
$$n^2R = \frac{a^2g}{16K^2} = .96.$$

(The actual amplitude is .0008 of that observed at the eyepiece.)

TABLE I.
Large Rocker and Long Handle.
(n^2R calculated = .96.)

Temp. C.	R in cms.	n .	n^2R .	Temp. C.	R in cms.	n .	n^2R .
110	4.8×10^{-4}	55	1.45	130	4.6×10^{-4}	$43\frac{1}{2}$	1.06
135	12.0 "	34	1.38	100	4.8 "	47	1.06
120	4.0 "	56	1.25	105	4.8 "	53	1.32
190	9.6 "	38	1.38	135	4.0 "	55	1.21
150	8.8 "	40	1.41	150	7.2 "	47	1.58
125	5.6 "	58	1.88	190	9.6 "	$37\frac{1}{2}$	1.33
165	8.0 "	44	1.55	170	8.8 "	47	1.94
175	1.6 "	69	0.74	175	8.4 "	46	1.76
205	10.0 "	$37\frac{1}{2}$	1.76	175	10.0 "	41	1.72

* This is the formula which Chuckerbutti derived, tested, and found wanting.

TABLE II.
Large Rocker and Short Handle.

Temp. C.	R in cms.	<i>n</i> .	<i>n</i> ² R.	Temp. C.	R in cms.	<i>n</i> .	<i>n</i> ² R.
240	10.4×10^{-4}	41	1.74	130	4.8×10^{-4}	47	1.06
200	8.0 "	45	1.62	145	4.8 "	56	1.50
100	4.0 "	58	1.34	105	1.6 "	$44\frac{1}{2}$	0.32
190	5.6 "	53	1.57	140	4.0 "	58	1.34
180	4.8 "	53	1.48	200	1.6 "	65	0.67
150	3.6 "	59	0.35	150	5.6 "	54	1.64
155	4.4 "	58	1.47	120	4.0 "	57	1.30
105	4.0 "	56	1.25	160	5.6 "	51	1.45
200	10.0 "	39	1.52	120	2.2 "	52	0.59
225	9.6 "	40	1.53	190	6.4 "	43	1.01

TABLE III.
Small Rocker and Long Handle.

Temp. C.	R in cms.	<i>n</i> .	<i>n</i> ² R.	Temp. C.	R in cms.	<i>n</i> .	<i>n</i> ² R.
180	3.6×10^{-4}	60	1.29	190	7.2×10^{-4}	$16\frac{1}{2}$	1.98
160	6.4 "	$17\frac{1}{2}$	1.96	120	2.8 "	68	1.29
160	8.0 "	40	1.28	155	8.8 "	41	1.48
200	2.4 "	49	0.58	180	2.0 "	51	0.52
115	4.0 "	61	1.48	105	2.0 "	90	1.62
175	2.8 "	61	1.04	128	8.0 "	39	1.20
115	2.4 "	76	1.38	105	2.0 "	93	1.72
130	4.0 "	53	1.13	105	3.2 "	61	1.58
145	5.6 "	45	1.13	180	12.8 "	34	1.48
185	5.6 "	54	1.62	160	4.0 "	65	1.69
115	3.2 "	61	1.19	245	6.4 "	46	1.35
130	3.2 "	58	1.06	180	2.0 "	88	1.55
155	3.6 "	$58\frac{1}{2}$	1.22	110	3.2 "	60	1.15

TABLE IV.
Small Rocker and Short Handle.

Temp. C.	R in cms.	<i>n</i> .	<i>n</i> ² R.	Temp. C.	R in cms.	<i>n</i> .	<i>n</i> ² R.
105	7.2×10^{-4}	40	1.15	200	12.0×10^{-4}	$32\frac{1}{2}$	1.28
240	12.0 "	36	1.55	160	6.4 "	$47\frac{1}{2}$	1.28
160	12.0 "	$37\frac{1}{2}$	1.68	100	2.0 "	92	1.70
180	3.2 "	61	1.18	170	4.8 "	60	1.73
150	5.6 "	53	1.57	190	3.6 "	70	1.76
195	2.4 "	70	1.17	100	2.0 "	98	1.93
150	3.2 "	56	1.00	150	4.0 "	59	1.38
95	2.0 "	92	1.70	180	3.2 "	70	1.57
120	2.4 "	96	2.21	185	4.0 "	58	1.35
200	9.6 "	34	1.11	190	4.0 "	50	1.00
165	7.2 "	$41\frac{1}{2}$	1.23	200	10.4 "	$37\frac{1}{2}$	1.48
140	3.2 "	65	1.35				

From these results it may be seen that :

(1) n^2R is fairly constant, though rather higher than the calculated value. If a graph be drawn, it is found that the values of n^2R for the small rocker lie fairly along the curve $n^2R=1.2$.

(2) an alteration of the length of the handle does not affect the average value of n^2R , nor does it affect the range of frequency.

(3) amplitudes are greater at higher temperatures, though this is probably dependent on the excess temperature of the copper over the lead, not on the actual temperature of the former.

Results with Simplified Rockers.

The difference between the calculated and average experimental values of n^2R obtained from prismatic rockers may be due to an imperfect knowledge of the value of K for such a shape. Accordingly a simpler form was devised, consisting of a cylindrical rod of copper with a groove cut from one end to within $\frac{1}{2}$ in. of the other. It had a peg in the centre of one end, so that, by resting the peg on a knife-edge, the bar rocked very nearly about its axis.

In the following tables (V.-VII.), frequencies greater than 130 were more conveniently found by sonometer. Most of those lying between 100 and 130 were estimated by both methods to serve as a check; they differed by less than 1 per cent. In estimating the constancy of the values of n^2R in the last column, it must be remembered that amplitudes are correct only to 0.4×10^{-4} .

The form of this simple rocker makes it easy to calculate its frequency under *elastic* vibration, treating it as a bar supported at both ends. These vibrations may be longitudinal, torsional, or transverse.

(1) Longitudinal :

$$\text{velocity} = \sqrt{Y/\rho} = 3 \times 10^5 \text{ cm./sec. at } 100^\circ \text{ C.}^*$$

(2) Torsional :

$$\text{velocity} = \sqrt{n/\rho} = 2 \times 10^5 \text{ cm./sec. at } 100^\circ \text{ C.}$$

Dividing either of these velocities by $2l$, where l is the length of the bar, we get frequencies running into thousands

* The values of Y and rigidity are from Wertheim Pogg. *Ann.* lxxviii. p. 381 (1849).

TABLE V.

Cylindrical Rocker, $\frac{1}{2}$ in. diameter.

$$2a = \cdot 32 \text{ cm.}; r = \cdot 625 \text{ cm.}; K^2 = \frac{1}{2}r^2 = \cdot 195 \text{ cm.}^2;$$

$$\text{whence } n^2R = 8\cdot 0.$$

(a) Length 22 cm. Weight 240 gms.

Temp. C.	R in cms.	<i>n</i> .	<i>n</i> ² R.	Temp. C.	R in cms.	<i>n</i> .	<i>n</i> ² R.
210	$5\cdot 6 \times 10^{-4}$	173	16·8	105	$2\cdot 4 \times 10^{-4}$	248	14·7
145	4·0 "	198	15·7	145	4·0 "	193	15·0
115	1·6 "	270	11·7	130	4·0 "	201	16·3
165	4·8 "	188	17·0	115	3·6 "	234	19·7
145	4·8 "	206	20·3	105	3·2 "	240	18·4
140	4·0 "	225	20·3	95	3·2 "	253	20·5
120	3·6 "	240	20·7	140	5·6 "	192	20·2
130	4·4 "	211	19·6	120	2·4 "	206	10·3
110	3·2 "	234	17·5	145	4·0 "	197	15·5
105	4·8 "	173	14·4	190	4·0 "	167	11·2
170	4·8 "	180	15·6	170	3·2 "	187	11·2
140	2·4 "	201	10·1	160	3·2 "	200	12·8

(b) Length 17 cm. Weight 190 gms.

160	$3\cdot 2 \times 10^{-4}$	211	14·2	160	$4\cdot 0 \times 10^{-4}$	200	16·0
150	3·2 "	222	15·7	145	3·2 "	222	15·7
135	3·2 "	236	13·9	120	2·4 "	255	15·6
150	3·2 "	222	15·7	105	2·0 "	263	13·8
125	2·0 "	234	11·0	160	3·2 "	222	15·7
115	2·0 "	248	12·3	160	3·2 "	217	15·0
195	3·2 "	197	12·4	170	4·0 "	201	16·2
170	3·2 "	211	14·5	200	0·8 "	345	9·6
115	1·6 "	259	10·3	135	3·2 "	228	16·6
125	2·0 "	234	10·9	115	0·8 "	345	9·6

(c) Length 12 cm. Weight 140 gms.

115	$1\cdot 6 \times 10^{-4}$	240	9·2	185	$1\cdot 8 \times 10^{-4}$	60	6·6
125	2·4 "	200	9·6	130	2·8 "	184	15·5
90	2·8 "	168	7·7	110	3·2 "	196	9·9
90	2·4 "	130	7·6	120	2·0 "	200	8·0
110	2·4 "	182	7·9	170	8·0 "	132	13·9
170	12·8 "	68	5·9	100	2·4 "	192	8·8
160	4·0 "	177	12·5	115	1·6 "	220	8·2
205	3·2 "	188	11·7	240	12·0 "	90	9·7
160	12·0 "	90	9·6	160	10·4 "	92	8·8
100	2·4 "	188	8·0	115	1·6 "	216	11·4
200	24·0 "	16	7·1	120	6·4 "	140	13·4

TABLE VI.

Cylindrical Rocker, $\frac{3}{4}$ in. diameter.

$$2a = .32 \text{ cm. ; } r = .95 \text{ cm. ; } K^2 = \frac{1}{2}r^2 = .45 \text{ cm.}^2 ;$$

$$\text{whence } n^2R = 3.5.$$

(a) Length 23 cm. Weight 520 gms.

Temp. C.	R in cms.	n .	n^2R .	Temp. C.	R in cms.	n .	n^2R .
120	8.0×10^{-4}	57	2.6	90	2.4×10^{-4}	140	4.7
105	4.0 "	92	3.4	170	4.0 "	114	5.2
90	3.2 "	114	4.1	135	2.4 "	140	4.7
130	3.2 "	126	5.1	140	8.0 "	60	2.9
180	2.4 "	123	3.6	125	4.0 "	98	3.8
165	3.2 "	111	3.9	200	4.0 "	92	3.4
150	3.6 "	114	4.8	180	2.4 "	130	4.1
135	2.4 "	133	4.2	165	5.6 "	74	3.1
145	2.0 "	154	4.7	215	6.0 "	80	3.7
115	5.6 "	89	4.4	165	4.0 "	96	3.7

(b) Length 17 cm. Weight 400 gms.

170	4.8×10^{-4}	70	2.3	115	6.0×10^{-4}	62	2.8
140	5.6 "	75	3.1	110	2.4 "	160	6.2
130	3.2 "	117	4.4	150	4.0 "	133	7.1
120	3.2 "	133	5.7	150	3.2 "	142	6.5
100	2.4 "	137	4.5	105	2.8 "	109	3.3
180	3.2 "	120	4.6	95	3.2 "	109	3.8
160	3.2 "	133	5.7	180	4.0 "	136	7.4
130	3.2 "	108	3.7	130	3.6 "	109	4.3
115	4.0 "	89	3.2	120	4.4 "	81	2.9
130	6.4 "	62	3.4	115	4.8 "	67	2.2

(c) Length 12 cm. Weight 280 gms.

190	2.0×10^{-4}	133	3.5	150	4.0×10^{-4}	139	7.2
175	2.8 "	112	3.5	130	4.0 "	150	9.0
160	2.8 "	124	4.3	110	2.4 "	120	3.5
125	8.0 "	52	2.3	150	3.6 "	91	3.0
120	1.6 "	154	4.7	135	2.8 "	137	5.3
105	4.0 "	107	4.6	120	6.4 "	66	2.8
100	3.6 "	104	3.9	150	5.6 "	64	2.3
180	2.4 "	130	4.1	105	3.2 "	100	3.2

TABLE VII.

Cylindrical Rocker, 1 in. diameter.

$$2a = \cdot 32 \text{ cm.}; r = 1\cdot 27 \text{ cm.}; K^2 = \cdot 78 \text{ cm.}^2;$$

$$\text{whence } n^2R = 2\cdot 0.$$

(a) Length 23 cm. Weight 970 gms.

Temp. C.	R in cms.	<i>n</i> .	<i>n</i> ² R.	Temp. C.	R in cms.	<i>n</i> .	<i>n</i> ² R.
180	$12\cdot 0 \times 10^{-4}$	35	1·5	105	$2\cdot 4 \times 10^{-4}$	108	3·0
160	9·6 "	53	2·7	140	2·4 "	64	1·5
145	8·0 "	57	2·8	120	3·2 "	66	1·4
130	4·8 "	63	1·9	105	4·0 "	64	1·6
100	3·2 "	65	2·1	180	2·4 "	98	2·3
95	2·4 "	78	1·5	150	4·4 "	66	1·9
200	4·4 "	63	1·7	185	16·0 "	32	1·6
185	3·6 "	72	1·9	175	13·6 "	35	1·6
160	8·0 "	56	2·5	165	7·2 "	46	1·5
130	4·0 "	65	1·7	130	4·0 "	66	1·7
95	4·0 "	63	1·6	90	3·2 "	70	1·6

(b) Length 17 cm. Weight 720 gms.

145	$5\cdot 6 \times 10^{-4}$	63	2·2	115	$2\cdot 8 \times 10^{-4}$	90	2·3
130	2·4 "	80	1·5	116	3·6 "	80	2·3
125	1·6 "	96	1·5	110	2·4 "	$92\frac{1}{2}$	2·0
180	$22\cdot 4$ "	30	2·0	110	2·0 "	102	2·1
170	8·0 "	41	1·3	135	8·0 "	49	1·9
160	6·4 "	47	2·6	120	3·2 "	74	1·7
150	3·2 "	66	1·4	115	4·0 "	80	2·6
155	4·0 "	60	1·2	110	2·4 "	109	2·9
145	4·4 "	75	2·5	115	5·6 "	60	2·0
100	2·4 "	70	1·2	135	12·0 "	52	3·0
145	4·0 "	68	1·8	120	8·8 "	56	3·4

(c) Length 12 cm. Weight 520 gms.

140	$5\cdot 2 \times 10^{-4}$	53	1·4	135	$3\cdot 2 \times 10^{-4}$	66	1·4
130	1·6 "	112	2·0	120	2·4 "	100	2·4
200-160	2·4 "	88	1·9	105	1·6 "	106	1·8
190	16·0 "	30	1·4	195	15·6 "	40	2·5
170	12·0 "	35	1·5	170	9·6 "	44	1·8
135	2·8 "	80	1·8	160	2·4 "	88	1·9
120	2·4 "	91	2·0	145	4·0 "	62	1·5
105	1·6 "	109	1·8	170	6·4 "	46	1·3
100	4·4 "	82	2·9	160	5·6 "	53	1·6
180	3·4 "	72	1·8	110	1·2 "	98	1·1
110	2·0 "	93	1·7	115	2·4 "	90	1·9

As none of those in the tables exceeds 350, these kinds of vibrations are out of the question.

(3) Transverse :

$$N = V_{\text{long}} \frac{9}{8} \frac{K}{l^2} \text{ is the lowest frequency possible.}$$

The calculated values for n (transverse) are given below:—

TABLE VIII.

Summary of Results for Cylindrical Rockers.

Radius r in cms.	Length l in cms.	n^2R .		Calculated Transverse Frequency n .		Experimental Range of n .	
		Calc.	Experi- mental average.				
				At 100°.	At 200°.		
.625	22	8.0	16.1	304	227	270 to	173
"	17	"	13.7	508	380	345 to	197
"	12	"	9.5	1004	765	240 to	60
.95	23	3.5	4.0	472	423	140 to	57
"	17	"	4.3	865	773	160 to	62
"	12	"	4.2	1735	1555	154 to	52
1.26	23	2.0	1.9	622	357	108 to	32
"	17	"	2.0	1135	1020	109 to	30
"	12	"	1.8	2282	2075	112 to	30

It can be seen that the calculated and experimental values of n^2R are in agreement, save in the first two lines (unaccountably), and that the actual range of frequencies is considerably below that required by elastic vibrations (transverse).

The effect of varying the width of the groove while the diameter and length of the bar were kept constant was next examined.

According to the "gravity" formula, n^3R should be proportional to a^2 . The first two sections of Table IX. give good confirmation of this, as the average value of n^2R is quadrupled when the width of the groove is doubled; when the latter is increased half as much again, as in (c), the average value of n^2R is only increased in the ratio 37 : 22, instead of 9 : 4. Rockers with wide grooves are difficult to start, especially if heavy, and do not oscillate well.

It has long been known that pressing or weighting the bar raises the pitch, because the rocker cannot oscillate so far; observations made during the above experiments show that the amplitude is correspondingly reduced.

TABLE IX.

Rod 1.9 cm. diam., $13\frac{1}{2}$ cm. long.(a) $2a = .24$ cm.

Temp. C.	R in cms.	n.	n^2R .	Temp. C.	R in cms.	n.	n^2R .
160	9.6×10^{-4}	45	1.9	170	8.8×10^{-4}	45	1.8
135	10.4 "	40	1.7	100	5.6 "	56	1.8
100	3.2 "	83	2.2	95	4.8 "	86	4.3
135	5.6 "	60	2.0	170	9.6 "	45	1.9
140	1.6 "	137	3.0	130	4.8 "	60	1.7
105	4.8 "	63	1.0	210	24.0 "	24	1.4
130	19.6 "	34	2.3	110	11.2 "	45	2.4
110	3.2 "	84	2.2	140	1.6 "	120	2.3
135	5.6 "	78	3.4	145	20.2 "	35	2.4
175	10.4 "	43	1.9	100	2.8 "	89	2.2

Average value of $n^2R = 2.2$: calculated 2.0.(b) $2a = .48$ cm.

130	1.6 "	228	10.4 "	170	3.2 "	150	7.4
230	4.0 "	150	9.0 "	190	5.6 "	139	10.8
145	5.6 "	170	13.4 "	200	4.8 "	142	9.7
170	2.4 "	151	5.5 "	205	5.6 "	147	12.1
180	8.4 "	92	6.7 "	190	5.2 "	149	11.5
—	2.4 "	132	4.2 "	—	2.4 "	146	5.1

Average value of $n^2R = 8.8$: calculated 7.9.(c) $2a = .32$ cm.

150	2.8 "	137	5.2 "	120	6.4 "	66	2.8
115	3.2 "	117	4.4 "	115	3.2 "	100	3.2
190	7.2 "	55	2.2 "	170	11.2 "	51	2.9
170	6.8 "	59	2.4 "	135	3.2 "	100	3.2
150	5.6 "	64	2.3 "	130	6.4 "	66	2.8
135	2.8 "	133	5.0 "	170	24.0 "	35	2.9
120	3.2 "	137	6.0 "	125	6.4 "	62	2.5
136	8.0 "	60	2.9 "	115	4.8 "	117	6.6
125	4.0 "	110	6.3 "	95	3.2 "	107	4.0

Average value of $n^2R = 3.7$: calculated 3.5.

Harmonics of the simple vibration have also been observed in the microscope. Sondbauss and Chuckerbutti's experiments show that these are due to the independent vibration on one ridge alone, taking place at the same time as the more usual rocking from ridge to ridge.

Vibration of the lead block was prevented as far as possible during the above experiments. The intensity of the sound does not depend merely on the amplitude of the rocking, but is amplified by the block, if the latter is in a

condition to do so. Using a hollow lead cylinder for the rocker to work on, Dinkler* found the character of the sound changed by putting weights inside the former.

Conclusion.

The results show that the formula— n^2R constant for a given rocker—satisfies the observed phenomena fairly well. As n^2R has been shown to be proportional directly to a^2 , and inversely to K^2 , it is to be concluded that the gravity theory is the more correct one. Such deviations as occur are at small amplitudes (less than about .0002 cm. for the simple form of rocker), and it is possible that some other form of oscillation is to be found here. No common form of elastic vibration, whether longitudinal, torsional, or transverse, can be present, as the frequencies are not of the required order, nor do they vary with temperature in the manner required by the theory of elastic vibrations.

Finally, the author wishes to express his obligation to Prof. C. H. Lees, of East London College, for bringing Mr. Chuckerbutti's paper to his notice, and for valuable ideas, utilized in this work.

C. On the Theory of δ -Radiation.

By P. L. KAPITZA †.

WHEN an alpha particle strikes a solid body, electrons are emitted from the place of collision and form the so-called δ -radiation. The explanation of the phenomenon is usually given as follows:—

When the particle penetrates into the body, it loses its kinetic energy in ionizing atoms of the body. The liberated electrons possess certain speeds, and after several collisions may escape from the surface. These escaped electrons form the δ -radiation. Such a consideration, however, gives only the general picture of the phenomenon, and is insufficient to provide a basis for any numerical calculations. But if we consider the phenomenon purely from a statistical point of view, we can easily obtain some numerical values for the speeds and numbers of electrons in the δ -radiation.

Let us first assume that the alpha particle, when stopped, liberates all its energy to heat up a very small volume of the body. It can be easily calculated that the temperature at this place of local heating may reach several thousand

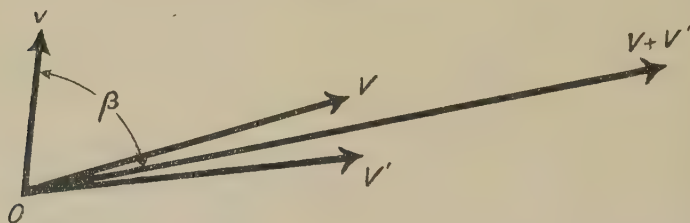
* *Repertorium de Phys.* iv. p. 131 (1868).

† Communicated by Sir Ernest Rutherford.

degrees. From the heated surface of the body, thermionic emission will take place. This thermionic emission is the δ -radiation. This process will last a very short time, due to the fact that the heat will quickly dissipate into the body; but it will be shown in this paper that the δ -radiation calculated from such a picture of the phenomenon gives the right value both for the number of electrons emitted and for their speeds.

Let us suppose that the collision between an α -particle and an atom takes place at O (see fig. 1); then the relations

Fig. 1.



which hold between the velocities of the α -particle before and after collision (written V and V' respectively) and the velocity v of the liberated electron are

$$M(V - V') = mv, \quad \dots \dots \dots (1)$$

$$\frac{1}{2}M(V^2 - V'^2) = \frac{1}{2}mv^2, \quad \dots \dots \dots (2)$$

where M is the mass of the α -particle and m the mass of the electron. Equation (2) may be re-written as

$$M(V - V')(V + V') = mv^2,$$

where the left-hand side of the equation is a scalar product of two vectors. If we call the angle between these vectors β and substitute $(V - V')$ from (1) we have

$$\cos \beta = \frac{|v|}{|V + V'|}.$$

Now it is known that an α -particle loses by ionization only a very small portion of its energy, and maintains its direction of motion practically unaltered. Thus we may say that $V + V'$ is practically equal to $2V$, and thus

$$\cos \beta = \frac{|v|}{2|V|} \quad \dots \dots \dots (4)$$

If we assume a definite speed for the α -particle, the value of the speed of the electron can be calculated for a given value of β . The results of such calculations are shown in Table I.

TABLE I.

Speeds of the ionized electrons, in volts.

β .	Distance from the end of the α -ray range.		
	7 cm.	3.5 cm.	1.5 cm.
0°	4190	2620	1340
30°	3150	1900	1005
60°	1048	630	335
80°	126	76	40
85°	32	19	10
90°	0	0	

The energy of the ionized electron is expressed in volts for α -particles with ranges 7.0, 3.5, 0.5, and 1.5 cm. in air. Now, if the α -particle at each collision loses energy corresponding to a fall of potential of 40 volts, we see from the table that the value of β for the liberated electrons will lie between 85° and 80°. This means that the velocity of the liberated electron is very nearly perpendicular to the path of the α -particle. If this were so, the electrons produced by an α -particle striking a surface vertically could never escape from that surface without an alteration in the direction of their velocity. Such an alteration would only be produced as a result of inter-electronic collisions.

These collisions would result in a transference of energy from electron to electron, and thus after the passage of an α -particle we have a great number of electrons moving with different speeds and in different directions. This process of the interchange of energy between the electrons will result in the liberation of electrons from the surface.

Now we shall make an attempt to calculate the amount of δ -radiation to be expected, using the known constants of emission formula of Richardson.

From the ordinary data of thermionic emission, we know what is the chance for an electron to escape from the body if it has the average kinetic energy corresponding to a certain temperature. We may assume that after the passage of the α -particle into the solid the ionized electrons remain in a cylinder of small cross-section and possess kinetic energy equal to that lost by the α -particle. This energy is dissipated along the radius of this cylinder according to the ordinary laws of thermal conductivity, while from the cross-section of the cylinder which coincides with the surface of

the body electrons are emitted according to Richardson's law.

The above assumptions are, however, open to criticism. In the first place, the Richardson formula is only true when a Maxwell distribution of electron velocities exists. In our problem this will not be the case, but it is quite probable that, using the Richardson formula, we shall obtain results which are of the correct order of magnitude. In the second place, immediately after the passage of the α -particle only a few thousands of electrons possess very large kinetic energy, and the application of thermal-conductivity constants which have only a statistical mean value is open to criticism in the case of a small volume. But if we bear in mind that in practice we deal with the average value of δ -radiation produced by a very large number of collisions, then the adoption of the ordinary thermal conductivity is probably nearly correct.

Let us take the path of the α -ray as the axis of a cylindrical system of coordinates. Let also the α -particle enter the body at right angles to the surface. Then, in the first moment after the passage of the α -particle, all the energy yielded to the body will be included in a cylinder which we shall take as infinitely thin. In this way we may state the initial conditions of the problem. Thus if T is the temperature, t the time, and r the distance from the axis, we have:

$$\begin{aligned} t = 0, \quad T = 0, \quad r \neq 0; \\ t = 0, \quad T = \infty, \quad r = 0. \end{aligned}$$

The ordinary thermal - conductivity equation may be written

$$r \frac{\partial T}{\partial t} = \frac{K}{cd} \frac{\partial}{\partial r} r \frac{\partial T}{\partial r}, \quad \dots \quad (5)$$

where K , c , and d are the thermal conductivity, thermal capacity, and density of the body respectively. To find a particular solution of this equation which will satisfy the initial conditions, we shall introduce a new variable u such that

$$u = \frac{r^2}{t}. \quad \dots \quad (6)$$

Equation (5) will then take the form

$$u \frac{dT}{du} = -\frac{4K}{cd} \frac{d}{du} u \frac{dT}{du}; \quad \dots \quad (7)$$

and this, after integration, gives

$$T = D \int_0^{\frac{cd}{4K} \cdot \frac{r^2}{t}} \frac{e^{-y}}{y} dy, \quad (8)$$

where D is a constant.

By differentiating this particular solution with respect to t , we find a solution which will satisfy the initial conditions :

$$T = \frac{D}{t} e^{-\frac{cd}{4K} \cdot \frac{r^2}{t}}. \quad (9)$$

To determine the constant D in this expression (9), we may express the fact that an amount of heat Q , equivalent to the amount of energy lost by the α -particle per unit length of path, passes through unit length of the surface of a cylinder coaxial with the origin during the time from $t=0$ to $t=\infty$. This is done by the expression

$$Q = -2\pi K \int_0^\infty r \frac{\partial T}{\partial r} dt. \quad (10)$$

Thus, using (9) and performing the integration, we get

$$D = \frac{Q}{4\pi K}; \quad (11)$$

and the required solution of equation (5) is therefore

$$T = \frac{Q}{4\pi K t} e^{-\frac{cd}{4K} \cdot \frac{r^2}{t}}. \quad (12)$$

According to the laws of thermionic emission, the number of electrons emitted per unit surface of the heated body during one second is given by

$$N = AT^{\frac{1}{2}} e^{-\frac{b}{T}}, \quad (13)$$

where A and b are experimentally-determined constants*. Now, if we sum the right-hand side of the expression (13) over all possible values of r and t , the number of electrons emitted by the collision of an α -particle will be

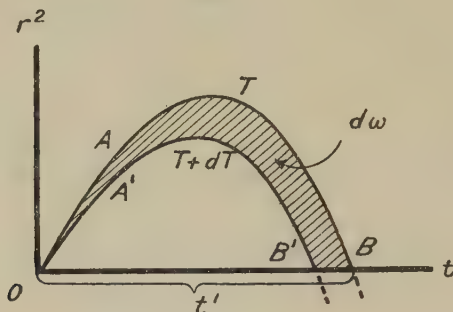
$$N = \int_0^\infty \int_0^\infty \pi A T^{\frac{1}{2}} e^{-\frac{b}{T}} dr^2 dt. \quad (14)$$

To perform the integration in (14), by substituting for T

* See Richardson's book, 'The Emission of Electricity from Hot Bodies.'

from (12) we get a very complicated expression. But the difficulty can be overcome in the following way:—Let us take two coordinate axes for the variables r^2 and t , as shown in fig. 2. Then the meaning of our integration may be

Fig. 2.



interpreted as follows. Each surface element of the area included between the two axes will be multiplied by

$$f(r, t) = \pi A T^{\frac{1}{2}} e^{-\frac{b}{T}}$$

and the whole summed. Now let us divide the surface into elements ($d\omega$) over which the temperature may be taken as constant. For this purpose we take T as constant in the expression (12), and, varying r^2 and t , we draw the curve OAB . Afterwards we draw another curve $OA'B'$ for a temperature equal to $T + dT$. Then the hatched surface $OABB'A'$ will be equal to the element of the surface ($d\omega$) with constant temperature.

It is easy to see that

$$d\omega = \frac{d \int_0^{t'} r^2 dt}{dT} dT, \quad \dots \dots (15)$$

where t is the uppermost limit of integration determined from the point of intersection of the curve OAB with the axis t . The value of t is obtained from (12) by putting $r^2 = 0$. Thus

$$t' = \frac{Q}{4\pi K T}. \quad \dots \dots (16)$$

If we introduce in (15) the value of r^2 from (12), we get

the following expression for $d\omega$:

$$d\omega = \frac{Q^2}{8\pi^2 KcdT^3}, \quad \dots \dots \dots (17)$$

and the number of electrons emitted will be

$$dN = AT^{\frac{1}{2}} e^{-\frac{b}{T}} \pi d\omega = \frac{AQ^2}{8\pi Kcd} T^{-5/6} e^{-\frac{b}{T}} dT. \quad \dots \dots (18)$$

After performing the integration with respect to T from 0 to ∞ we get

$$N = \frac{1}{16\sqrt{\pi}} \cdot \frac{A}{b^{3/2}} \cdot \frac{Q^2}{cdK}. \quad \dots \dots \dots (19)$$

From this formula we can get an estimate of N . For this purpose we may take the polonium α -particle, which has energy $2.09 \cdot 10^{-13}$ cal. and a range of $7.03 \cdot 10^{-4}$ cm. in platinum. Then

$$Q = 2.98 \cdot 10^{-10} \text{ cal./cm.}$$

Taking for c , d , and K the ordinarily accepted values from the tables, we get

$$N = 2.12 \cdot 10^{-20} \frac{A}{b^{3/2}}.$$

Now the values of b and A vary very much with the conditions of the surface of the platinum. Taking the lowest and the highest value*, we get the following results :—

TABLE II.

	A.	C.	N.	Volt.
Richardson	7.5×10^{25}	4.43×10^4	0.15	2.5
„	5.0×10^{28}	6.8×10^4	59.0	3.5
Langmuir	2.02×10^{31}	8.0×10^4	19,000	4.1

In the first two columns are the values for A and b , and in the third the number of emitted electrons. We see that N will vary very much, from 0.15 to 19,000.

The actual values of N obtained from experiments on δ -radiation lie between the values given above, and, as has been shown by Pound† and Bumstead & McGougan‡,

* Value taken from Richardson, *loc. cit.* p. 81.

† Pound, *Phil. Mag.* xxiii. p. 813 (1912).

‡ Bumstead & McGougan, *Phil. Mag.* xxiv. p. 462 (1912).

depend very much on the conditions of the surface, and vary in the same way as the thermionic radiation; for instance, the presence of hydrogen occluded in the surface diminishes the δ -radiation as well as the thermionic emission. The conditions under which the experiments on δ -radiation were performed are similar to those in which Richardson obtained the values of A and b ; and here we have a numerical agreement with the theoretical results. The value for N obtained from Langmuir's data is enormous, but Langmuir worked in extremely high vacuum, in which no δ -ray experiments have been made. According to this theory we should expect also an increase in the δ -radiation when high-vacuum conditions are reached.

Other facts observed in connexion with δ -radiation phenomena may be explained by this theory. For instance, it has been observed that the source of α -rays itself emits many more electrons of the δ -radiation per α -particle than a plate which the α -particles hit after leaving the source. The explanation of this phenomenon may be as follows:—If the α -particle strikes the body at a small glancing angle, the electrons would be emitted from a larger surface because the cross section of the cylinder increases with decreasing glancing angle. Now there will be α -particles going back, at all glancing angles to the surface, into the metal plate which carries the radioactive substance, whereas all the α -particles which hit an external plate do so nearly at right angles to the surface. So we may expect more δ -radiation to come from the source itself than from an external plate. Also, if an α -particle is slipping on the surface of the source, then some of the ionized electrons which have velocities perpendicular to the path of the α -rays as well as to the surface could escape from the source at a speed which may be high. This explanation may account for the high-speed electrons observed from the sources by Bumstead and McGougan* and Wertenstein†.

The speed of the greater number of the δ -radiation electrons, according to the approximate measurements of Hauser‡, is less than 6 volts, and the distribution of speeds is Maxwellian. We can, from the formula (18), get an estimate of the most probable speed of the emitted electrons. For this purpose we have to find the temperature at which the largest number of electrons is emitted. This is by

* *Loc. cit.*

† *Le Radium*, ix. p. 6 (1912).

‡ *Physikalische Zeitschrift*, p. 936, 1912.

differentiating (18) thus :

$$\frac{d^2N}{dT^2} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

which gives for T the value

$$T = \frac{2}{5} b.$$

The energy in volts of the emitted electrons which corresponds to this temperature is given in the fourth column of Table II., and lies between 2.5 and 4.1 volts. So again we see that the theory is in agreement with experiment.

From the above discussion we may assume that the radiation, in general, has the same origin as thermionic emission, the difference being that in the case of thermionic emission the energy is supplied to the electrons by heating, while in the case of δ -radiation the energy is supplied by the α -particle. The calculations made above are not rigid enough to enable us to get a very close numerical agreement between theory and practice, but are sufficient to show that the δ -radiation may be explained using the same constants as are used in the case of thermionic emission. The enormous influence of the conditions of the surface on the magnitude of both types of radiation makes a more detailed calculation useless.

The same method of calculation may be applied to the case of a positive ray or to a beam of electrons which, striking a solid surface, produces a secondary emission of slow electrons. In this case slow-moving particles strike a body, but they do not penetrate deep in the surface. The heat given up by the entering particle at the first instant must be considered as concentrated in a point and afterwards dissipated in the body perpendicularly to a spherical surface. The problem may be treated in the same way as the previous one, only using spherical co-ordinates instead of cylindrical ones.

The solution will be

$$T = \frac{Q'}{4\pi^{\frac{3}{2}}} \sqrt{\frac{cd}{K^3}} \cdot \frac{1}{\sqrt{t^3}} e^{-\frac{cd}{4K} \cdot \frac{r^2}{t}}, \quad . \quad . \quad . \quad (21)$$

where Q' is the total energy of the particle which enters the body.

Performing the integration as before, we find a more complicated expression for N :

$$N = \frac{A}{\sqrt{32\pi}} \cdot \frac{Q'^{\frac{4}{3}}}{K \sqrt{cd}} \int_0^\infty \frac{e^{-\frac{b}{T}}}{T^{11/6}} dT. \quad . \quad . \quad . \quad (22)$$

The most probable speed of the emergent electrons calculated in the same way as (20), (21) comes to

$$T = \frac{6}{11} b.$$

This means that the most probable energy of the emergent electrons will be 1.36 times the value found in the previous case. See (20).

If we consider electrons or positive rays with gradually increasing penetrative power, we proceed gradually from expression (22) to the expression (19). This means that for a certain depth of penetration the number of the emitted secondary electrons stops increasing. This is actually found to be the case experimentally.

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CI. *Tensors of given Types in Riemann Space.*

By PHILIP FRANKLIN*.

ONE method of arriving at the laws of nature which describe certain phenomena, which has been given prominence by the theory of relativity, consists in deciding on the degree of mathematical complexity required, writing down the most general expressions of this degree of complexity, and using some of the known characteristics of the phenomena to specialize or reduce in number the constants entering into this expression. If the result obtained explains the known experiments in the field under discussion, it is accepted as a physical law; if not expressions of greater complexity are tried†.

According to the theory of relativity, all physical laws are, in their mathematical expression, statements of the equality of tensors. Consequently it becomes of importance to determine what tensors of given types are possible, and the object of the present paper is to prove a series of theorems useful in this connexion. A few examples of their application are added.

* Communicated by the Author. Presented to the American Mathematical Society, Dec. 27, 1922.

† The point of view here adopted, while in the main that of most writers on relativity, is in the precise form given the outcome of a series of discussions in the Seminar of Professors L. P. Eisenhart and O. Veblen at Princeton University.

We shall first consider tensors in Euclidean space, referred to Cartesian coordinates. That is, the transformations admitted are linear orthogonal ones, which leave the bilinear form

$$\delta_{ab}x^ay^b \dots \dots \dots (1)$$

(δ_{ab} equals 1 or 0 according as a is or is not equal to b) invariant. If we define an *arithmetic* tensor as one whose components are constant, being independent of both the position of the point and the particular set of Cartesian coordinates used; then we have:—

THEOREM I. *There are no non-vanishing arithmetic tensors of odd order; every arithmetic tensor of even order ($2p$) may be expressed as a linear combination of products of p tensors of type (1).*

Proof. Consider the arithmetic tensor

$$A_{abc\dots}x^ay^bz^c\dots \dots \dots (2)$$

For the special choice of vectors $x^i = \delta_{1i}$, $y^i = \delta_{2i}$, $z^i = \delta_{3i}$ (i from 1 to n , the dimensionality of the space), its value is

$$A_{123\dots} \dots \dots \dots (3)$$

If the index 1 appears an *odd* number of times in this term, then on using new coordinates which only differ from the old in having the direction of the 1-axis reversed, our vectors will have the same components as before except that x^1 (and any other non-zero 1-component) will have its sign changed. Consequently the value of the tensor for this choice of coordinates will be

$$-A_{123\dots} \dots \dots \dots (4)$$

and since the value of a tensor is independent of the coordinates, we must have this term equal to 0. By a similar argument, we may show that any component of a tensor which involves any index an odd number of times must be zero. Since every component of a tensor of odd order must contain at least one index an odd number of times, if such a tensor is arithmetic, all of its components must be zero, which is the first part of our theorem.

For tensors of even order, we shall only state the proof in detail for the case of sixth order tensors; the method is, however, general. If our tensor is

$$A_{abcdef}x^ax^by^bz^cu^dv^ew^f \dots \dots \dots (5)$$

the tensor has the value zero ; while on rotating the axes as before, the components are

$$\begin{aligned}x=y=z=u &= (\sqrt{\frac{1}{2}} \quad \sqrt{\frac{1}{2}} \quad 0 \quad 0 \quad \dots), \\v=w &= (-\sqrt{\frac{1}{2}} \quad \sqrt{\frac{1}{2}} \quad 0 \quad 0 \quad \dots),\end{aligned}$$

and its value is

$$\frac{1}{8} B_{111111} + \frac{1}{8} B_{222222} = \frac{1}{4} B_{111111}, \quad \dots \quad (11)$$

which shows that all the B's are zero, and completes the proof.

THEOREM II. *If a set of numerical constants has the property that the linear functions of the components of any tensor of the n th order with these as coefficients are the components of a tensor of the m th order, then these numerical constants are the components of two arithmetic tensors of the $m+n$ th and m th orders respectively ; the tensor of the m th order is formed by multiplying the tensor of the n th order by the arithmetic tensor of the $m+n$ th order, contracting with respect to its n indices, and adding the arithmetic tensor of the m th order.*

We state the proof for the case $m=n=2$. If Q_{ab} is the tensor of the m th order to be formed, and A_{cd} is the arbitrary tensor of the n th order, we may write

$$Q_{ab} = p_{abcd} A_{cd} + q_{ab}, \quad \dots \quad (12)$$

where the p 's and q 's are the numerical constants. Since A is an arbitrary tensor, we may take it as identically zero, which shows that the q_{ab} are the components of a tensor, necessarily arithmetic. Therefore

$$Q_{ab} - q_{ab} = P_{ab} = p_{abcd} A_{cd} \quad \dots \quad (13)$$

is a tensor. If we replace the arbitrary A_{cd} in this last equation by the product of two vectors, and multiply both members by the product of two new arbitrary vectors, we obtain :

$$P_{ab} u^a v^b = p_{abcd} x^c y^d u^a v^b. \quad \dots \quad (14)$$

The left member of this equation is an invariant, and since the right member is the product of p_{abcd} by four arbitrary vectors, it follows that the p 's are transformed like the components of a tensor of the fourth order, and since they are constant, they must be the components of an arithmetic tensor.

As an application of this theorem, we consider the expressions for the stresses in a viscous fluid. We assume

that the terms in the stress tensor due to the viscosity depend linearly on the special derivatives of the velocity $\partial u_c / \partial x_d$ (which are the components of a tensor of the second order since the velocity u_c is a vector); and that the terms in these derivatives vanish for a symmetric dilatation, *i. e.* in case $\partial u_c / \partial x_d = k \delta_{cd}$.

Since the stress tensor is of the second order, by theorems I. and II. it must be of the form :

$$S_{ab} = A \delta_{ab} + (B \delta_{ab} \delta_{cd} + C \delta_{ac} \delta_{bd} + D \delta_{ad} \delta_{bc}) \partial u_c / \partial x_d. \quad (15)$$

Since S_{ab} must be symmetric in a and b , we have $C = D$, and our condition about the vanishing of the last terms for a dilatation gives :

$$3B + C + D = 3B + 2C = 0. \quad (16)$$

This shows that

$$S_{ab} = A \delta_{ab} + C \{ (\partial u_a / \partial x_b + \partial u_b / \partial x_a) - \frac{2}{3} \sum_c \partial u_c / \partial x_c \delta_{ab} \}, \quad (17)$$

the ordinary expression where A is the pressure in the absence of friction, and C is the negative of the coefficient of viscosity. The above is a modified form of the derivation given by Einstein in his Princeton Lectures*.

In setting up the equations of gravitation and other equations in the general theory of relativity, we are led to form invariants and tensors which, from the analogous expressions in the Newtonian theory, we expect to be linear in the second derivatives of the components of the fundamental quadratic tensor (g_{ij}) as these components correspond to the Newtonian potential. This gives importance to the following theorems, which deal with the most general forms for tensors of given orders in Riemann space, linear in these second derivatives.

As these tensors are all found to depend on the curvature tensor, we shall collect here a few of the fundamental expressions related to it. In terms of the Christoffel symbols:

$$\Gamma_{bc}^a = \frac{1}{2} g^{as} \left(\frac{\partial g_{cs}}{\partial x_b} + \frac{\partial g_{bs}}{\partial x_c} - \frac{\partial g_{bc}}{\partial x_s} \right), \quad (18)$$

not themselves tensors, we define the following expressions, which may be proved to be tensors :

$$R_{bcd}^a = \left(\frac{\partial \Gamma_{bd}^a}{\partial x_c} - \frac{\partial \Gamma_{bc}^a}{\partial x_d} \right) + (\Gamma_{rc}^a \Gamma_{bd}^r - \Gamma_{rd}^a \Gamma_{bc}^r), \quad (19)$$

$$R_{bc} = R_{bca}^a, \quad (20)$$

$$R = g^{bc} R_{bc}. \quad (21)$$

* A. Einstein, 'The Meaning of Relativity,' Princeton, 1923, p. 22.

For a "geodesic coordinate system at a point," i. e. one in which, at the point in question, $g_{ij} = \delta_{ij}$, $\partial g_{ij} / \partial x_k = 0$, we have :

$$R_{bcd}^a = \frac{1}{2} \left(\frac{\partial^2 g_{bc}}{\partial x_a \partial x_d} + \frac{\partial^2 g_{ad}}{\partial x_b \partial x_c} - \frac{\partial^2 g_{ac}}{\partial x_b \partial x_d} - \frac{\partial^2 g_{bd}}{\partial x_a \partial x_c} \right), \quad (22)$$

$$R_{bc} = \frac{1}{2} \left(\frac{\partial^2 g_{bc}}{\partial x_a \partial x_a} + \frac{\partial^2 g_{aa}}{\partial x_b \partial x_c} - \frac{\partial^2 g_{ac}}{\partial x_a \partial x_b} - \frac{\partial^2 g_{ab}}{\partial x_a \partial x_c} \right), \quad (23)$$

$$R = \frac{\partial^2 g_{bb}}{\partial x_a \partial x_a} - \frac{\partial^2 g_{ab}}{\partial x_a \partial x_b}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

at the origin of the geodesic coordinate system.

Concerning invariants in Riemann space, we have :

THEOREM III. *The most general invariant involving the g_{ij} 's, together with their first and second derivatives, and these last linearly, is a linear function of the Riemann scalar curvature, R ; i. e., $AR + a$, where A and a are constants*.*

By hypothesis, the invariant sought must be of the form :

$$I = U + V_{ab,cd} \frac{\partial^2 g_{ab}}{\partial x_c \partial x_d}, \quad . \quad . \quad . \quad . \quad (25)$$

where U and the V 's are functions of the g_{ij} and of their first derivatives. From the symmetry of the g_{ij} and of their second derivatives it follows that the $V_{ab,cd}$ may be taken to be symmetric in the pairs of indices ab and cd without real loss of generality.

If, at a point in our space, we introduce a geodesic coordinate system, we shall have

$$g_{ij} = \delta_{ij}, \quad \partial g_{ij} / \partial x_k = 0, \quad . \quad . \quad . \quad . \quad (26)$$

at the point, and (25) becomes

$$I = a + b_{ab,cd} \frac{\partial^2 g_{ab}}{\partial x_c \partial x_d}, \quad . \quad . \quad . \quad . \quad (27)$$

where the b 's and a are now constants, independent of the point selected. (27) must be an invariant under all transformations which do not disturb the conditions (26). But, for a linear orthogonal transformation we have :

$$\left. \begin{aligned} x_i &= p_{ij} \bar{x}_j \quad \text{where} \quad \delta_{ab} p_{ai} p_{bk} = \delta_{ik}, \\ \bar{g}_{ik} &= g_{ab} p_{ai} p_{bk} \quad \text{since} \quad \bar{g}_{ik} \bar{x}_i \bar{x}_k = g_{ab} x_a x_b, \\ \partial g_{ik} / \partial \bar{x}_r &= \partial g_{ab} / \partial x_c p_{ai} p_{bk} p_{cr}, \end{aligned} \right\} . \quad . \quad (28)$$

and hence such transformations do leave (26) invariant.

* The proof here given was suggested by that of H. Weyl, see his *Raum, Zeit, Materie*, fourth edition, p. 287.

But since, for such transformations, we also have

$$\partial^2 \bar{g}_{ik} / \partial \bar{x}_r \partial \bar{x}_s = \partial^2 g_{ab} / \partial x_c \partial x_d p_{ai} p_{bk} p_{cr} p_{ds}, \quad (29)$$

the second derivatives in (27) are transformed like the components of a tensor, and hence the b 's must be the components of an arithmetic tensor (Theorem II.), and by Theorem I. we must have

$$b_{ab,cd} = A \delta_{ab} \delta_{cd} + B \delta_{ac} \delta_{bd} + C \delta_{ad} \delta_{bc}. \quad (30)$$

The conditions of symmetry make $B=C$, giving:

$$b_{ab,cd} = A \delta_{ab} \delta_{cd} + B (\delta_{ac} \delta_{bd} + \delta_{ad} \delta_{bc}). \quad (31)$$

But (26) also remains true if we subject the coordinates to the transformation

$$x_a = \bar{x}_a + \frac{1}{6} P_{a,bcd} \bar{x}_b \bar{x}_c \bar{x}_d, \quad (32)$$

where the P 's are an arbitrary set of constants, symmetrical in b, c , and d ; for this gives:

$$\left. \begin{aligned} \partial x_a / \partial \bar{x}_i &= \delta_{ai} + \frac{1}{2} P_{a,icd} \bar{x}_c \bar{x}_d, \\ \bar{g}_{ik} &= \partial x_a / \partial \bar{x}_i \partial x_b / \partial \bar{x}_k g_{ab} \\ &= (\delta_{ai} + \frac{1}{2} P_{a,icd} \bar{x}_c \bar{x}_d) (\delta_{bk} + \frac{1}{2} P_{b,kcd} \bar{x}_c \bar{x}_d) g_{ab}. \end{aligned} \right\} \quad (33)$$

For the transformation (32), we also have, for the origin,

$$\partial^2 \bar{g}_{ab} / \partial \bar{x}_c \partial \bar{x}_d = \partial^2 g_{ab} / \partial x_c \partial x_d + P_{a,bcd} + P_{b,acd}, \quad (34)$$

as is easily seen from (33). Therefore, since (27) remains invariant under such transformations, we must have

$$b_{ab,cd} (P_{a,bcd} + P_{b,acd}) = 2b_{ab,cd} P_{a,bcd} = 0. \quad (35)$$

In particular, if we take $P_{a,bcd} = \delta_{a1} \delta_{b1} \delta_{c1} \delta_{d1}$, and combine (31) and (35), we obtain

$$A + 2B = 0; \quad B = -\frac{1}{2}A. \quad (36)$$

Therefore (27) can be written

$$I = A (\partial^2 g_{aa} / \partial x_b \partial x_b - \partial^2 g_{ab} / \partial x_a \partial x_b) + a, \quad (37)$$

or in virtue of (24)

$$I = AR + a. \quad (38)$$

Hence our invariant can be put in this form at any point for the special coordinates chosen, and since this is known to be an invariant for constant values of A and a , it is so expressible in any coordinates.

THEOREM IV. *The most general covariant tensor of the second order involving the g_{ij} 's, together with their first and*

second derivatives, and these last linearly, is a linear combination of R_{ik} , Rg_{ik} , and g_{ik} *.

We have by hypothesis :

$$T_{gh} = U_{gh} + V_{gh, ab, cd} \partial^2 g_{ab} / \partial x_c \partial x_d, \quad (39)$$

where the U 's and V 's are functions of the g 's and their first derivatives, and the latter are symmetric in the pairs of indices ab and cd . As before, on introducing a geodesic coordinate system, we have for the origin :

$$T_{gh} = a_{gh} + b_{gh, ab, cd} \partial^2 g_{ab} / \partial x_c \partial x_d \quad (40)$$

As this must be a tensor for linear orthogonal transformations, and for such transformations (29) holds, we have by theorem II. that a_{gh} is an arithmetic tensor of the second order (δ_{gh}) and $b_{gh, ab, cd}$ is one of the sixth order. Hence by theorem I. we must have, in view of the symmetry :

$$\left. \begin{aligned} b_{gh, ab, cd} = & A(\delta_{gh} \delta_{ab} \delta_{cd}) + B(\delta_{gh} \delta_{ac} \delta_{bd} + \delta_{gh} \delta_{ad} \delta_{bc}) \\ & + C(\delta_{ab} \delta_{cg} \delta_{dh} + \delta_{ab} \delta_{ch} \delta_{dg}) + D(\delta_{cd} \delta_{ag} \delta_{bh} + \delta_{cd} \delta_{ah} \delta_{bg}) \\ & + E(\delta_{ag} \delta_{bc} \delta_{hd} + \delta_{bg} \delta_{ac} \delta_{hd} + \delta_{ag} \delta_{bd} \delta_{hc} + \delta_{bg} \delta_{ad} \delta_{hc}) \\ & + F(\delta_{ah} \delta_{bc} \delta_{gd} + \delta_{bh} \delta_{ac} \delta_{gd} + \delta_{ah} \delta_{bd} \delta_{gc} + \delta_{bh} \delta_{ad} \delta_{gc}). \end{aligned} \right\} \quad (41)$$

By using (32) and (34) in the same way as before, we find

$$b_{gh, ab, cd} P_{a, bcd} x^g y^h = 0, \quad (42)$$

since $T_{gh} x^g y^h$ is an invariant, and (32) leaves the components of the arbitrary vectors x and y , situated at the origin, unchanged. As the P 's in (42) are arbitrary, except for their symmetry in b, c , and d , we may obtain various relations between the constants in (41) by taking special values. Taking $x^i = y^i = \delta_{2i}$, $P_{a, bcd} = \delta_{a1} \delta_{b1} \delta_{c1} \delta_{d1}$ gives :

$$A + 2B = 0; \quad (43)$$

$x^i = y^i = \delta_{1i}$, $P_{a, bcd} = \delta_{a1} \delta_{b1} \delta_{c1} \delta_{d1}$ gives

$$A + 2B + 2C + 2D + 4E + 4F = 0; \quad (44)$$

$x^i = \delta_{2i}$, $y^i = \delta_{1i}$, $P_{a, bcd} = \delta_{a2} \delta_{b1} \delta_{c1} \delta_{d1}$ gives :

$$D + 2E = 0; \quad (45)$$

and finally $x^i = \delta_{1i}$, $y^i = \delta_{2i}$, $P_{a, bcd} = \delta_{a2} \delta_{b1} \delta_{c1} \delta_{d1}$ gives :

$$D + 2F = 0. \quad (46)$$

* This theorem is stated by Weyl (*loc. cit.*). The theorem is discussed by M. v. Laue, *Die Relativitätstheorie* (1921 edition, vol. ii. p. 100f.) He fails to consider the term g_{ik} , which is independent of the second derivatives.

It follows from the last four equations that

$$A = -2B; \quad C = D = -2E = -2F. \quad . \quad . \quad (47)$$

This shows that (40) may be written :

$$\left. \begin{aligned} T_{gh} = & \delta_{gh} A (\partial^2 g_{aa} / \partial x_b \partial x_b - \partial^2 g_{ab} / \partial x_a \partial x_b) \\ & + C (\partial^2 g_{gh} / \partial x_a \partial x_a + \partial^2 g_{aa} / \partial x_g \partial x_h - \partial^2 g_{ah} / \partial x_a \partial x_g \\ & - \partial^2 g_{ag} / \partial x_a \partial x_h) + K \delta_{gh}. \end{aligned} \right\} \quad (48)$$

But, according to (23) and (24) this is the value of

$$T_{gh} = A R_{gh} + 2 C R_{gh} + K g_{gh} \quad . \quad . \quad (49)$$

in the coordinates chosen. Since g_{gh} and R_{gh} are known to be covariant tensors, this must represent the tensor T in any coordinates, and the theorem is proved.

By the aid of theorem IV. we may easily arrive at Einstein's law of gravitation as the generalization of Poisson's equation for the Newtonian theory :

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = 4\pi k \rho. \quad . \quad . \quad (50)$$

In the generalization, we will replace the density of matter ρ by the energy tensor T_{gh} ; consequently for the left member we seek a tensor of the second order in the coefficients of the fundamental quadratic tensor (g_{ij}) which take the place of the single potential ϕ , and their derivatives. By analogy with (50) we expect the tensor to be linear in the second derivatives, and hence by theorem IV. our equation must be of the form (49) or

$$R_{gh} + s R g_{gh} + t g_{gh} = k T_{gh} \quad . \quad . \quad (51)$$

after a change of constants. Since it is known that the divergence of the tensor T_{gh} vanishes ($\partial T_{gh} / \partial x_h = 0$, in geodesic coordinates) this must be true for the left member of (51). But its divergence (in geodesic coordinates) is

$$(\frac{1}{2} + s) (\partial^3 g_{aa} / \partial x_b \partial x_b \partial x_g - \partial^3 g_{ab} / \partial x_a \partial x_b \partial x_g), \quad . \quad (52)$$

as is seen from (23) and (24). This shows $s = -\frac{1}{2}$. To interpret the meaning of t , we multiply (51) by g^{gh} and sum for both indices. We thus obtain

$$\left. \begin{aligned} R + 4s R + 4t &= k T_{gh} g^{gh}, \\ \text{or} \quad 4t - R &= k T_{gh} g^{gh}. \end{aligned} \right\} \quad . \quad . \quad (53)$$

Hence, at points for which $T_{gh} = 0$, R has the constant value $4t$, and if we call this value R_0 , (51) may now be written :

$$R_{gh} - \frac{1}{2} R g_{gh} + \frac{1}{4} R_0 g_{gh} = k T_{gh}. \quad . \quad . \quad (54)$$

In his earlier papers Einstein assumed $R_0=0$, later* he considered the general case. The derivation of (54) just given is similar to that given by Einstein in his Princeton Lectures †.

THEOREM V. *The most general tensor of the fourth order involving the g_{ij} 's together with their first and second derivatives and these last linearly has as its covariant components a linear combination of R_{efgh} ($g_{es}R^s_{fgh}$), $g_{ef}R_{gh}$, $g_{ef}g_{gh}R$, $g_{ef}g_{gh}$ and the terms which can be formed from them by permuting the indices.*

We assume our tensor is

$$T_{efgh} = U_{efgh} + V_{efgh, ab, cd} \partial^2 g_{ab} / \partial x_c \partial x_d, \dots (55)$$

and as before consider the form in geodesic coordinates :

$$T_{efgh} = a_{efgh} + b_{efgh, ab, cd} \partial^2 g_{ab} / \partial x_c \partial x_d. \dots (56)$$

By reasoning similar to that used for theorem IV. we show that a_{efgh} and $b_{efgh, ab, cd}$ are arithmetic tensors ; also that

$$b_{efgh, ab, cd} P_{a, bcd} x^e y^f z^g u^h = 0 \dots (57)$$

for an arbitrary choice of P's (symmetric in bcd), x, y, z , and u .

Consider the terms in $b_{efgh, ab, cd}$ which contain δ_{ef} and write them collectively as $\delta_{ef} q_{gh, ab, cd}$. If we take $x^i = y^j = \delta_{i3}$, $z^3 = u^3 = 0$, and give the P's such values that they are zero if a, b, c , or d are 3, the only non-zero terms in (57) will be

$$q_{gh, ab, cd} P_{a, bcd} z^g u^h = 0. \dots (58)$$

We may apply to this equation the same argument we used on (42) above, as the q here is an arithmetic tensor with the same symmetry properties as the b of (42), and our restriction on the zero components when the indices are three is consistent with the values there used. Thus we may show the part of (55) resulting from $\delta_{ef} q_{gh, ab, cd}$ is of the form (cf. (49)) :

$$A g_{ef} g_{gh} R + C g_{ef} R_{gh} + K g_{ef} g_{gh}, \dots (59)$$

and a similar argument would apply to the terms involving a δ which contained both indices from the four $e f g h$. Thus the sum of all such terms corresponds to a part of (55) which is a tensor, and from now on we may confine our

* A. Einstein, "Kosmologische Betrachtungen zur allgemeinen Relativitätstheorie," *Sitzungsber. der Preuss. Akad. d. Wiss.* 1917, p. 142.

† *L. c.* p. 92.

remarks to the tensor left when this is subtracted from our original tensor. The corresponding part of b contains the following terms, where the coefficients are equal as indicated because of the symmetry :—

$$\left. \begin{aligned} & G(\delta_{ae}\delta_{bf}\delta_{cg}\delta_{dh} + \delta_{af}\delta_{cg}\delta_{dh} + \delta_{ae}\delta_{bf}\delta_{ch}\delta_{dg} + \delta_{af}\delta_{be}\delta_{ch}\delta_{dg}) \\ & + H(\delta_{ag}\delta_{bh}\delta_{ce}\delta_{df} + \delta_{ah}\delta_{bg}\delta_{ce}\delta_{df} + \delta_{ag}\delta_{bh}\delta_{cf}\delta_{de} + \delta_{ah}\delta_{bg}\delta_{cf}\delta_{de}) \\ & + I(\delta_{af}\delta_{bg}\delta_{ce}\delta_{dh} + \delta_{ag}\delta_{bf}\delta_{ce}\delta_{dh} + \delta_{af}\delta_{bg}\delta_{ch}\delta_{de} + \delta_{ag}\delta_{bf}\delta_{ch}\delta_{de}) \\ & + J(\delta_{ae}\delta_{bh}\delta_{cf}\delta_{dg} + \delta_{ah}\delta_{be}\delta_{cf}\delta_{dg} + \delta_{ae}\delta_{bh}\delta_{cg}\delta_{df} + \delta_{ah}\delta_{be}\delta_{cg}\delta_{df}) \\ & + K(\delta_{af}\delta_{bh}\delta_{ce}\delta_{dg} + \delta_{ah}\delta_{bf}\delta_{ce}\delta_{dg} + \delta_{af}\delta_{bh}\delta_{cg}\delta_{de} + \delta_{ah}\delta_{bf}\delta_{cg}\delta_{de}) \\ & + L(\delta_{ae}\delta_{bg}\delta_{cf}\delta_{dh} + \delta_{ag}\delta_{be}\delta_{cf}\delta_{dh} + \delta_{ae}\delta_{bg}\delta_{ch}\delta_{df} + \delta_{ag}\delta_{be}\delta_{ch}\delta_{df}) \end{aligned} \right\} \quad (60)$$

For this part alone we still have (57). If we take $x^i = \delta_{i2}$, $y^i = z^i = u^i = \delta_{i1}$ and $P_{a,bcd} = \delta_{a2}\delta_{b1}\delta_{c1}\delta_{d1}$, we obtain by combining (60) with (57):

$$G + J + L = 0. \quad \dots \dots \dots (61)$$

For $y^i = \delta_{i2}$, $x^i = z^i = u^i = \delta_{i1}$ and $P_{a,bcd} = \delta_{a2}\delta_{b1}\delta_{c1}\delta_{d1}$,

$$G + I + K = 0, \quad \dots \dots \dots (62)$$

and by taking in turn $z^i = \delta_{i2}$ and $u^i = \delta_{i2}$ we obtain similarly:

$$\left. \begin{aligned} & H + I + L = 0, \\ & \text{and} \quad H + J + K = 0 \end{aligned} \right\} \quad \dots \dots \dots (63)$$

These equations show that

$$G = H; \quad I = J; \quad K = L = -G - I, \quad \dots \dots (64)$$

and consequently the part of (56) corresponding to (60) is

$$\left. \begin{aligned} & gG(\partial^2 g_{ef}/\partial x_g \partial x_h + \partial^2 g_{gh}/\partial x_e \partial x_f \\ & \quad - \partial^2 g_{jh}/\partial x_e \partial x_g - \partial^2 g_{eg}/\partial x_f \partial x_h) \\ & + I(\partial^2 g_{gf}/\partial x_e \partial x_h + \partial^2 g_{eh}/\partial x_g \partial x_f \\ & \quad - \partial^2 g_{fh}/\partial x_e \partial x_g - \partial^2 g_{eg}/\partial x_f \partial x_h) \end{aligned} \right\} \quad (65)$$

Comparison with (22) shows that this expression may be written

$$\left. \begin{aligned} & G R_{efg}^h + I R_{gfe}^h \\ \text{or} \quad & G g_{hx} R_{efg}^x + I g_{hx} R_{gfe}^x \end{aligned} \right\}, \quad \dots \dots \dots (66)$$

as in the normal coordinate system the g 's are replaced by δ 's, and the second form is used since we are considering the covariant components of our tensor. (59) and (66) show

that our tensor may be written, with a change of notation for the constants :

$$\left. \begin{aligned} & AR_{hefg} + BR_{hgfe} + Cg_{ef}R_{gh} + Dg_{gh}R_{ef} \\ & + Eg_{eg}R_{fh} + Fg_{fh}R_{eg} + Gg_{eh}R_{fg} + Hg_{fg}R_{eh} \\ & + Ig_{ef}g_{gh}R + Jg_{eg}g_{fh}R + Kg_{eh}g_{fg}R \\ & + Lg_{ef}g_{gh} + Mg_{eg}g_{fh} + Ng_{eh}g_{fg} \end{aligned} \right\} \quad (67)$$

The tensor we have found may also be described as a linear combination of all the tensors of the fourth order which can be obtained by multiplying the curvature tensor R^e_{fgh} (or a scalar) by the fundamental quadratic tensor (g_{ij}) any number of times, and contracting to make the final order four. The tensors of this type not appearing explicitly in (67) are linearly dependent on those present in virtue of the relations :

$$R^e_{fgh} + R^g_{jhe} + R^h_{feg} = 0, \quad R_{ab} = R_{ba}, \text{ etc., } \dots \quad (68)$$

which follow from (22).

We conclude with the following generalization of the preceding three theorems, which includes them as special cases :—

THEOREM VI. *The most general tensor of given even order involving the g_{ij} 's and their first and second derivatives, these last linearly, is a linear combination of tensors which may be formed from the tensor R^e_{fgh} and the fundamental quadratic tensor (g_{ij}) by multiplication and contraction. There are no tensors of odd order of the type required.*

For the method used to separate out the terms in (59) above, may evidently be used to separate out *all* the terms for a tensor of order greater than four, and to reduce them to products of the fundamental quadratic tensor by those of the next lower even order. The last statement in the theorem follows from the non-existence of arithmetic tensors of odd order.

Theorems V. and VI. are believed to be new. They show that the complete theory of tensors of the type discussed depends on the curvature tensor R^e_{fgh} which plays the same role for these tensors that the fundamental quadratic tensor does for arithmetic tensors. The theorems are presented here not only for their mathematical interest, but because of their possible use in physical applications.

Harvard University.
Sept. 1922.

CII. *Directional Observations of Atmospherics—1916–1920.*
*By R. A. WATSON WATT, B.Sc., F.Inst.P.**

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I. *Source of Data.*

IN connexion with a Meteorological Office investigation into the Location of Thunderstorms by Radiotelegraphic Direction Finding, begun in 1915, Capt. C. J. P. Cave, R.E., then Meteorologist-in-charge at South Farnborough, was able to arrange, through the good offices of Captain Slee, R.N., that the coastal direction-finding stations of the Admiralty should supply reports of observations made, when the exigencies of the service permitted, on the strength and apparent direction of arrival of atmospherics. The purpose of this paper is to present the results of a statistical reduction of some of the data so obtained. Of twelve reporting stations, six were selected as having supplied data nearly continuously over a four-year period, these stations were:—

	Latitude.	Longitude.
Carnsore	52° 11' 50" N.	6° 21' 0" W.
Browhead	51° 27' 20" N.	9° 45' 30" W.
Lizard	49° 58' 55" N.	5° 12' 15" W.
Prawle	50° 13' 10" N.	3° 42' 40" W.
Flamborough	54° 07' 05" N.	0° 04' 55" W.
Peterhead	57° 33' 20" N.	1° 48' 55" W.

It will be noted that the stations form a fairly well extended network from S. Ireland to N.E. Scotland. The wave-length on which the observations were made was always short, and may be taken to be, on the average, some 400 metres.

The intensity of disturbance was reported on an arbitrary scale, it is not, however, proposed to discuss here anything other than the observed bearing, or apparent direction of arrival, of atmospherics. This was determined by the ordinary direction-finding method of estimation of relative signal strengths as the search-coil of a Bellini-Tosi radio-goniometer was rotated. The personnel of these stations developed amazing powers of aural discrimination in the application of this method, and the consistency of the data to be presented in the course of this report is a striking proof of their high skill applied to a peculiarly difficult and confusing type of direction finding. The variation of

* Communicated by the Author.

personnel from watch to watch, and transfers between stations, are believed to have nearly neutralized personal error as affecting comparison of observations from different periods and stations.

II. *Distribution of Data.*

Reporting began in March 1916, and the observations between that date and July 1920 are dealt with in this paper. The total number of observations discussed amounts to 12,973. Table O shows the distribution of these observations amongst stations and periods. For purposes of reduction the data have been grouped according to three-month seasons approximately centering on equinox or solstice, and according to a diurnal subdivision of four periods, morning, forenoon, afternoon, and evening. These periods were again grouped into "light" and "dark," and into "A.M." and "P.M." pairs. This classification was rendered necessary by the fact that observations were not made at fixed hours, but at any hour when atmospherics were prominent and when work permitted. Further, no observations were made between 2100 and 0400 G.M.T.

The result of these limitations, combined with the known higher intensity of atmospheric disturbance during the hours of darkness, is that a great majority of all observations fell close to the hours of 0600 and 2000 G.M.T.

III. *Most Frequent and Mean Directions of Maximum Disturbance.*

Frequency curves, showing the number of occasions on which a given azimuth from true North was reported as most disturbed, have been plotted for each station, for each of the subdivisions as to season, time of day, and illumination already mentioned. Typical curves are shown in fig. 1.

The directions forming the peaks of these frequency curves are tabulated as X_F in the summary of results, Table 1. They will be reviewed in some detail at a later point in this paper.

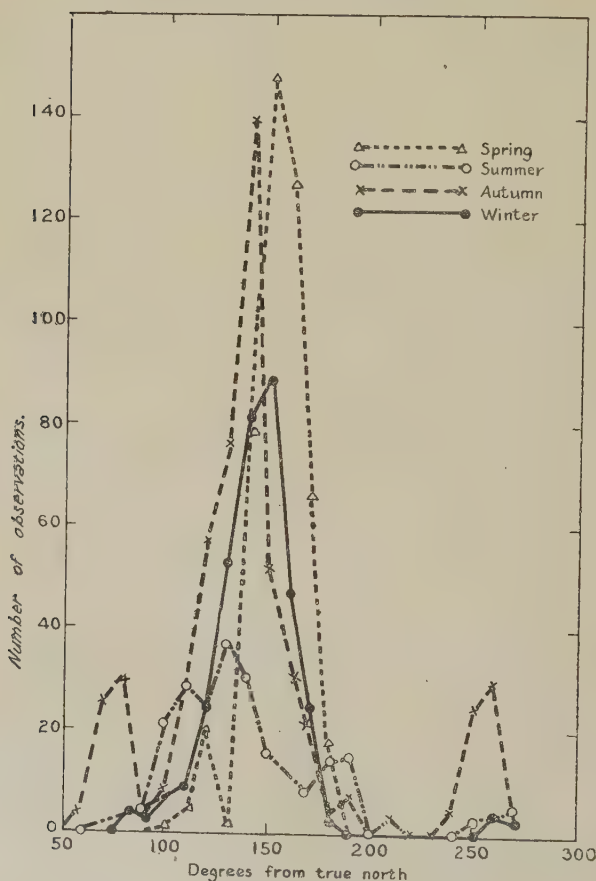
The whole of the observations are affected by the radio-goniometric ambiguity of 180° , since the direction-finder determines the vectorial direction without discrimination of sense. Thus an observation reported as 150° E. of N. may apply to disturbance originating $150^\circ + 180^\circ = 330^\circ$ E. of N. Actually this ambiguity is of small moment since, as mentioned in a previous communication*, all available

* "Directional Observations of Atmospherics, 1920-1921," Roy. Soc. Proc. A. 102, pp. 460-478 (1922).

evidence, both theoretical and observational, points to an overwhelming preponderance of origins in lower latitudes, *i.e.* of directions of arrival lying between 90° and 270°

Fig. 1.

Seasonal Frequency Curves, Flamborough.



(through 180°) E. of N. The present data in themselves support this interpretation, since simultaneous bearings taken at different stations almost invariably converge towards the South.

For statistical purposes, however, it has been considered that the most probable resolution of the ambiguity, in the

mass, would be to assign to all observations a sense such that the frequency curve has a peak directed in general, towards S.E. rather than N.W., and covers a range of 90° on either side of the peak. Thus, the average value of X_F being 150° , the frequency curves will in general extend from 60° to 240° E. of N., and to a reported bearing of 30° would be assigned the value 210° in this curve.

Table O	Station	Total.	midnight sunrise	sunrise noon	noon sunset	sunset midnight	sunrise sunset	sunset sunrise	midnight noon	noon midnight	Spring	Summer	Autumn	Winter
		T	m	f	a	e	L	D	AM	PM	P	M	A	W
Table I	Peterhead	1366	412	84	240	630	329	1037	500	866	428	201	424	313
	Flamborough	1549	394	102	283	760	196	1153	466	1063	465	243	495	346
	Carnsore	4299	1388	384	345	1582	1318	2981	1700	2533	1226	966	776	1331
	Browhead	2675	760	223	519	1173	743	1932	583	1692	746	453	711	765
	Prawle	1569	288	61	282	938	341	1228	348	1221	300	144	516	609
	Lizard	1515	261	38	323	893	364	1151	308	1207	302	175	484	554
		12973												
	Peterhead	157	159	140	143	153	141	156	159	153	160	139	150	150
	Flamborough	145	157	133	122	147	120	142	155	143	153	133	138	147
	Carnsore	149	152	147	143	147	144	150	151	148	148	153	157	148
	Browhead	139	159	132	137	139	137	139	159	138	138	99	133	140
	Prawle	153	158	173	95	152	95	153	168	152	153	93	127	153
	Lizard	148	163	95	92	148	90	150	166	148	148	89	122	148
	Peterhead	15110.6	159.9+0.9	129.4+3.5	118.1+1.7	15140.6	136.7+1.5	154+0.5	156.5+1.0	14840.7	161440.5	141.6+1.5	143.9+1.1	151.8+1.0
	Flamborough	1412+0.6	151.5+0.8	123+3.9	126.5+1.7	142.3+0.8	126+1.6	145.4+4.6	147.2+3.5	138.3+0.7	154+0.6	137.7+1.2	130.2+1.3	142.2+1.0
	Carnsore	14140.4	153.6+0.8	15.9+1.5	111+1.0	147.3+0.8	145.2+0.8	150+0.5	153.740.7	145.40.5	150.2+0.5	147.2+1.0	150+1.1	147.2+0.8
	Browhead	119.740.6	157.3+1.4	129.9+3.0	126.0+1.0	137+10.6	128.6+1.3	143.2+0.7	154.8+1.3	163.70.6	141.5+0.9	117.3+2.0	130.3+1.2	143.8+1.2
	Prawle	150.5+1.0	153.9+2.4	171.9+6.2	101.3+2.6	145.6+0.9	101.5+2.5	152.7+0.8	174+2.0	143+1.0	156.1+1.2	104.6+3.7	124+1.1	158.8+1.2
	Lizard	140.5+0.8	163.7+2.3	101.9+7.7	105.5+2.1	141.3+0.6	99.2+2.1	145+0.8	161+1.2	137.3+0.8	150.1+1.0	103.9+3.0	128.6+1.4	147.5+1.3
	Peterhead	21.7	17.7	33.8	25.8	15.3	28.3	16.7	23.6	20.2	10.6	21.4	22.8	18.2
	Flamborough	24.4	16.4	39.6	28.8	19.6	32.5	19.6	27.0	24.2	13.4	29.0	28.5	18.3
	Carnsore	27.9	30.0	30.1	30.3	22.3	30.6	26.2	29.6	26.1	18.7	31.5	29.1	31.2
	Browhead	32.6	37.8	43.9	36.4	20.9	36.5	30.0	39.6	26.6	25.6	45.0	32.3	32.0
	Prawle	38.6	38.6	44.7	44.2	27.2	47.7	32.4	39.1	34.8	20.3	45.0	43.1	30.1
	Lizard	30.9	36.9	47.7	40.7	20.5	41.5	26.4	38.2	30.9	16.6	41.9	31.2	30.4

The observations in each group having thus been assigned to the range $X_F \pm 90^\circ$ (or, actually, to the range $\pm 90^\circ$ from the 5° point nearest to X_F , this approximation being necessary to reduce the labour of computation) the mean direction of arrival of atmospherics has been computed for the group and tabulated as X_M . Since all the frequency curves are more or less skew, X_M does not coincide with X_F , and their difference is taken as a measure of the skewness.

It may be remarked that, while the most frequent or modal value X_F would doubtless be, in a perfect series of observations on a skew distribution, the most probable value of the variable sought for, yet psychological considerations would seem to point to the possibility of the mean value X_M bringing out the finer detail of variations. For it is the most frequent value that impresses itself on the memory of the actual observer, and predisposes him to assign to a dubious determination the value nearer to X_F , so that the curve becomes overweighted towards X_F ; the value of X_M , which emerges only after statistical reduction, while suffering

somewhat from this overweighting, is a more sensitive index of the true variation.

Along with each mean value is tabulated the standard error of the mean. The distribution not being normal, the "probable error" will not be equal to two-thirds of the standard error but the error in assuming that this is so, should it be preferred to think in terms of the "probable" error, will be small.

IV. *The Standard Deviations.*

The standard deviations from mode and mean have also been computed and those referred to the mode have been tabulated. In no case is the skewness sufficient to make these two deviations differ by any considerable amount. These standard deviations give a convenient (inverse) measure of the "peakiness" of the distribution curves, and their seasonal and diurnal variations are in themselves interesting on this account.

V. *Diurnal Variation.*

As has already been stated, the observations were not made at fixed hours. The diurnal variation has, accordingly, been examined by subdivision into four main groups:—*m* (morning) containing observations made between midnight and sunrise, *f* (forenoon) sunrise to noon, *a* (afternoon) noon to sunset, and *e* (evening) sunset to midnight. On the whole the observations are crowded at the boundaries between *m* and *f* and between *a* and *e*.

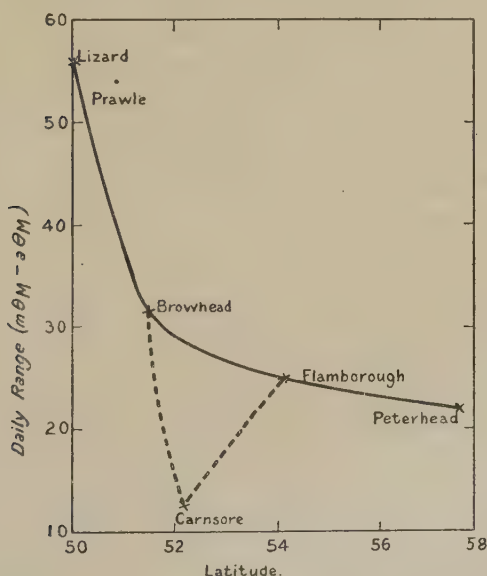
The unweighted mean of the most frequently disturbed directions for all six stations then varies from 160° in the morning, through 137° in the forenoon, to 122° afternoon, returning to 148° in the evening period. The use of mean values in place of modes does not appreciably alter these figures, which become 157° , 136° , 123° and 144° respectively. (It will, however, be noted that the skewness is greater during the dark hours.) There is, accordingly, a counter-clockwise swing of 34° range between morning and afternoon. The data from individual stations are as consistent as could be expected, the direction of swing being the same for all six in the periods *a* to *e* and *e* to *m*, slight swings opposite to those of the majority are shown by two stations in the period *f* to *a*, and by one in the period *m* to *f*. These irregularities are all within the range of probable error in the *f* and *a* groups, the "probable error" reaching 5° in some cases in *f*.

The diurnal range for each station may be specified by the quantity $({}_m\Theta_M - {}_a\Theta_M)$, *i.e.*, the difference between the mean values of the mean direction of arrival for the morning and afternoon groups. These quantities for the six stations are plotted in fig. 2, against the latitude of each station.

It will be seen that, excluding Carnsore, which shows, throughout the whole of the data, variations very much smaller than those at other stations, the range of diurnal variation decreases as the latitude increases.

Fig. 2.

Mean Daily Range of Mean Direction of Arrival of Atmospherics plotted against Latitude.

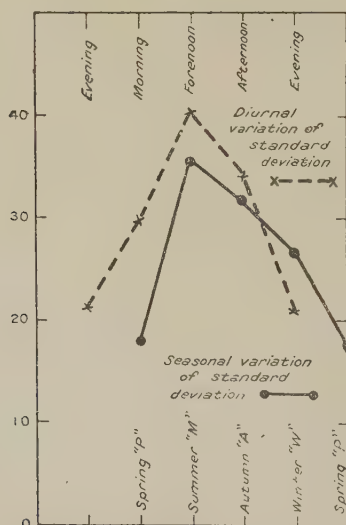


Proceeding from the range of variation in passing from one group to another, to the standard deviation, within the group, from the mode or mean for that group, we find a remarkable regularity in diurnal change. The standard deviation of the *f* group is, in five out of six cases (the exception being Carnsore), much higher than that of the *m* and *a* groups. In all cases the standard deviation of the *e* group is less than that of *f*, and also, for all stations except Flamborough, less than for the *m* group. Thus, with but slight exceptions, the standard deviation has a diurnal

variation of the type shown in fig. 3, which shows the unweighted means of standard deviations for all stations.

The standard deviations also show strongly the influence of latitude. Peterhead has the least standard deviation in each group, (save in one case where Flamborough is 1° lower) and the general run of each curve is that of increasing standard deviation with decreasing latitude till Prawle is reached, this station having the maximum standard deviation in three curves, its neighbour Browhead providing the fourth maximum. All four curves then show a sharp decrease in standard deviation as between Prawle and Lizard.

Fig. 3.



The grouping of the observations according to whether the sun was above or below the horizon at the time of observation shows that, on the mean of all stations, the apparent direction of arrival of atmospherics varies from 122° E. of N. in daylight to 148° in darkness. All six stations without exception show a shift in the same direction though of varying amount.

Similarly there is a difference of 13° between the mean modes of observations taken in the "A.M." period 0000 to 1200, and those in the "P.M." period 1200 to 2400, the "A.M." value being 160° , the "P.M." 147° . The means of the corresponding means are 159° and 141° . Again the

shift is in the same direction at all stations. The skewness of the "P.M." distribution is noteworthy.

The standard deviations in the "light" group are some 50 per cent. higher than in the "dark," those of the "A.M." group some 20 per cent. higher than those of the "P.M." group.

VI. *The Seasonal Variation.*

The seasonal variation in the unweighted mean of the modal values is from 150° in Spring (February, March, and April) to 118° in Summer, returning through 138° in Autumn and 148° in Winter. Using means in place of modes these figures become 152° , 125° , 136° , and 149° .

Measuring annual range, in a manner similar to that adopted for daily range, $P\Theta_M - M\Theta_M$, the difference between Spring and Summer means, we find again that, within the limits of the probable errors, the range decreases with increasing latitude, Carnsore again showing an abnormally small range. Actually the slight discrepancies between adjacent pairs of stations become still less if seasonal modes are used instead of means, in the diurnal range means were slightly more regular than modes.

The seasonal variation of standard deviation is very consistent. Each one of the six stations has a minimal standard deviation in Spring, all save Peterhead have maximal standard deviation in Summer, (the discrepancy in the Peterhead value is only 1°); the Autumn and Winter values are not very different, and are approximately midway between the Spring and Summer values.

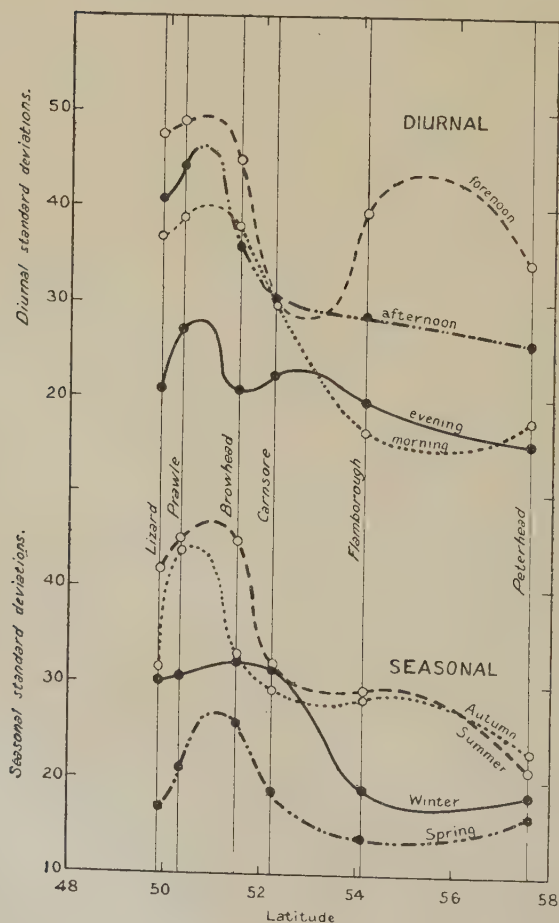
The variation with latitude of the seasonal standard deviations is in strict agreement with the variation of diurnal standard deviations, a general decrease of standard deviation with increasing latitude, Carnsore generally fitting into this scheme but showing slight irregularities, Lizard with consistently lower standard deviations than would follow from the general latitude law. Fig. 4 shows the curves of standard deviation against latitude for the four seasons.

The very uneven distribution in the diurnal groups prevents any clear evidence on diurnal variation of skewness from emerging. The seasonal distribution is, however, much more satisfactory, and the variation in skewness becomes fairly clear. If the difference $X_M - X_F$ be taken as measuring the amount of skew, then Spring shows a positive skew at all stations save the most Northerly one, Summer shows a larger positive skew, decreasing towards the North,

Autumn a positive skew in the South, becoming negative in the North, Winter a negative skew, most negative in the North. Thus Summer and low latitudes tend to give

Fig. 4.

Standard Deviations plotted against Latitude.



positive skews, Winter and high latitudes negative skews, a positive skew being here defined as a clockwise displacement of the mean value from the most frequent value.

VII. *Apparent Locations by Intersection.*

It is not proposed to discuss in this paper the apparent locations of centres of disturbance obtained by plotting on a gnomonic chart the nearly simultaneous observed bearings of atmospherics at several stations. Many such locations have been made, and many have been identified with thunderstorms independently reported by meteorological observers, but an examination of such locations must be reserved for another report.

It is, however, of interest to plot the various modes and means here tabulated. Dealing first with the modal values of all observations for each station, we find that all save Flamborough are contained in a band which, at the point where it cuts the 30° parallel of North Latitude, has a width of 3° , from $6^\circ 20' \text{ E.}$ to $9^\circ 20' \text{ E.}$ The width of the band contributed by the four south-westerly stations just covers the island of Majorca. Browhead, Lizard, and Prawle have modes which intersect at $38^\circ 30' \text{ N.}, 3^\circ 40' \text{ E.}$

The plotting of means instead of modes widens the band, the contribution of the four south-westerly stations now covering both Majorca and Minorca, Browhead, Carnsore and Prawle means intersect $35^\circ \text{ N.}, 6^\circ 20' \text{ E.}$

Of the seasonal values, the Spring modes (excluding Flamborough) form a narrow band crossing the 38° N. parallel between 6° and 8° E. , this being its narrowest section. The South-West group again give a band just within the width of Majorca. The corresponding means cross the 30° N. parallel between 6° and $8^\circ 30' \text{ E.}$, while the Browhead, Lizard, and Prawle means intersect at $38^\circ 5' \text{ N.}, 2^\circ 40' \text{ E.}$

The Summer modes are extremely scattered, the means give a diffuse group of intersections round $46^\circ 30' \text{ N.}, 10^\circ \text{ E.}$

The Autumn modes for Peterhead, Prawle, and Lizard intersect east of Corsica, at $42^\circ 15' \text{ N.}, 9^\circ 40' \text{ E.}$ The means give no intersection and show a slight tendency to converge in the N.W. quadrant.

The Winter modes for the four South-Western stations give a band just wider than Majorca, while Browhead, Lizard, and Prawle give an intersection at $37^\circ \text{ N.}, 4^\circ \text{ E.}$ The means are nearly parallel, the contributions from the South-Western group covering a region from just west of Majorca to just west of Ivica.

In the diurnal groups, the morning and afternoon modes are scattered, the forenoon modes from Prawle, Lizard, and Carnsore give a rather poor intersection at $49^\circ 45' \text{ N.}, 3^\circ 50' \text{ W.},$

the evening modes are nearly parallel. The morning means converge towards N.W., the forenoon means give two alternative intersections, Carnsore, Browhead, and Prawle at 48° N., 3° W., Carnsore, Lizard and Prawle at $49^{\circ} 30'$ N. $3^{\circ} 45'$ W. The afternoon means from Peterhead, Flamborough, Lizard, and Prawle intersect at $45^{\circ} 30'$ N., 14° E., the evening means from the four South-Westerly stations cross the 35° parallel between $7^{\circ} 20'$ and $8^{\circ} 5'$ E.

The "Light" modes from Lizard, Prawle, and Peterhead intersect at 49° N., 8° E., the 0 "Dark" means of Browhead, Carnsore, Lizard, and Prawle cross the 30° N. parallel at 7° and $9^{\circ} 15'$ E.

The "A.M." modes are nearly parallel, the "P.M." modes form a band whose narrowest section is 37° N., $4^{\circ} 20'$ to $5^{\circ} 5'$ E.

The "A.M." means are scattered, the "P.M." means from the four South-Western stations cross the 30° parallel between 10° and 14° E.

In almost all the cases noted above, it will be seen that Flamborough gives bearings pointing eastward of the main bands or intersections. This may be due to "refraction" by the nearly right-angled prism of land formed by Norfolk and Suffolk, some support is lent to this view by the fact that the three cases in which Flamborough falls into the general grouping are cases in which the bearing misses or just grazes this prism, although the cases of crossing to non-crossing are in the ratio of two to one.

The consideration of such refractions would, however, lead too far from the aim of the present paper, as the majority of the rays under consideration cross such land prisms at least once in passing from the Mediterranean to the observing stations.

VIII. *Harmonic Analysis.*

With a view to giving a more precise representation of the Seasonal variations discussed, monthly mean and modal values (without subdivision into diurnal groups) have been computed and the three sets of twelve ordinates, (X_F monthly most frequent direction of maximum disturbance, X_M monthly mean direction, and σ_F monthly standard deviation from X_F) analysed into the series

$$F = C_0 + C_1 \sin(\phi + X_1) + \dots + C_6 \sin 6(\phi + X_6),$$

where $X_6 = 15^{\circ}$. The coefficients and phase angles are set out in Table II. Their principal features are here enumerated. Owing to the marked disagreement between the

values for Carnsore and those for other stations the rough generalizations that follows are in some cases reached by neglecting Carnsore.

Fourier Coefficients														Approximate date of Maximum occurring nearest to June 15 th				
	Station.	C ₀	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	X ₁	X ₂	X ₃	X ₄	X ₅	1	2	3	4	5
Monthly most frequent direction of arrival	Peterhead	146	15	7	7	9	9	-3	217	95	25	10	66	Feb 5	Apr 26	June 20	June 27	July 9
	Flamborough	138	22	9	8	12	10	-7	215	87	38	3	70	Feb. 7	May 4	June 7	July 4	July 5
	Carnsore	152	6	4	1	2	4	-1	72	5	81	25	70	July 3	July 25	Apr. 26	June 12	July 5
	Browhead	129	14	10	6	5	15	+8	271	150	110	20	18	Dec 10	Aug. 29	July 25	June 17	June 1
	Prawle	130	36	16	9	3	6	-7	222	94	61	32	66	Feb. 1	Apr. 27	May 15	June 5	July 9
	Lizard	132	28	11	9	14	8	+1	246	126	115	85	70	Jan 6	Mar 26	July 20	July 12	July 5
Means of Coefficients		138	20	8	7	8	9	-2										
Monthly mean direction of arrival	Peterhead	146	12	3	4	6	7	0	223	125	8	12	66	Jan 29	Mar 27	July 7	June 25	July 9
	Flamborough	135	25	13	18	16	17	-9	210	82	30	4	65	Feb. 12	May 9	June 15	July 3	July 10
	Carnsore	150	4	2	4	2	1	-1	104	157	71	34	64	June 2	Aug 22	May 5	June 3	July 11
	Browhead	132	13	11	7	7	13	+4	266	161	107	13	15	Dec 15	Aug. 18	July 28	June 24	June 18
	Prawle	133	37	15	8	9	7	-2	225	90	54	21	0	Jan. 28	May 1	May 22	June 14	July 4
	Lizard	131	27	12	9	10	10	-3	247	142	100	87	64	Jan 5	Sept. 7	Aug. 4	July 10	July 10
Means of Coefficients		138	20	9	8	8	9	-2										
Standard deviation from monthly most frequent direction	Peterhead	18	5	8	3	5	3	+1	60	50	44	27	7	July 15	June 10	June 1	June 10	June 26
	Flamborough	23	10	7	4	2	4	-1	47	173	85	57	31	July 26	Aug 5	Apr. 21	May 11	June 3
	Carnsore	27	5	7	1	1	13	+1	0	39	26	54	16	Sept. 14	June 21	June 19	May 14	June 17
	Browhead	34	8	2	4	8	1	-3	62	150	62	14	58	July 13	Aug. 29	May 14	June 23	July 17
	Prawle	35	16	4	3	4	4	0	44	52	74	37	55	July 31	June 8	May 2	May 31	July 20
	Lizard	30	9	6	5	1	3	0	42	50	77	38	45	Aug 2	June 10	Apr. 29	May 30	May 19
Means of Coefficients		28	9	6	3	3	5	0										

(a) Most Frequent and Mean Directions of Arrival.

The constant term C_0 varies between 129° for Browhead, and 152° for Carnsore, the mean values do not depart from the modes by more than 3° , and the departures do not appear to be systematic. The considerable difference between the values of C_0 and the corresponding total values in Table I. arise from the very irregular distribution of observations from month to month, and consequent differences of weighting. The unweighted mean value for C_0 for all stations is 138° for both modes and means. This then may be accepted as an approximation to the mean direction of arrival of atmospherics in Great Britain.

The twelve month periodic term has an amplitude C_1 which (excluding the very small value for Carnsore) ranges between 12° and 37° , with a mean for all stations of 20° , again the same whether means or modes are used. The phase angles X_1 lie between 210° and 271° , the corresponding dates of incidence of maximum of this term lying about one month after the winter solstice. The lines of equal amplitude, in so far as they can be plotted with so few stations, have an inclination to the geographical meridians which is approximately midway between that of the isogonics and of the isoclinics of terrestrial magnetism, Peterhead and Browhead, Flamborough and Lizard, forming pairs of

similar amplitude, while Prawle has maximal amplitude. The phase angles X_1 , on the other hand, show a fairly strongly marked longitude variation, increasing Westerly longitude increasing the phase angle, *i. e.* giving an earlier date of maximum clockwise deviation. The actual dates of maximum range from December 10th for Browhead to February 7th for Flamborough in the case of X , for X_M the corresponding dates are December 15th and February 12th.

The same variation is found, with one exception other than Carnsore, in the phase angles X_2 of the six-month term. These indicate in X_F dates of maximum ranging from February 29th for Browhead to June 10th for Flamborough. In the case of X_m the dates of maximum are consistently earlier, by some three weeks on the average. The amplitudes, C_2 , of this term are, in general, less than half the corresponding amplitude C_1 .

The coefficients C_3, C_4 are all of the same order as C_2, C_5 tending to be somewhat larger than C_2 .

To sum up, the analysis reveals a well-marked annual variation, with a range of about 40° , such that the direction of arrival is approximately $138^\circ - 20^\circ = 118^\circ$ E. of N. one month after the summer solstice, and 158° E. of N. after the winter solstice. These deviations are greater in the S.E., less in the N.W., and are reached earlier in the W., later in the E.

The shorter period variations are relatively unimportant. The analysis does not throw much light on the skewness of the distribution. On the mean of all stations the series for X_F and X_M are almost undistinguishable, and the variation of skewness is more obvious in the coarser seasonal groupings previously discussed than in the monthly grouping.

(b) *Standard Deviations from Monthly Most Frequent Values.*

Here the constant term C_0 ranges from 18° at Peterhead to 35° at Prawle, small values of this measure of scattering pertaining to higher latitudes and *vice versa*. Carnsore fits into this general scheme, Lizard, as previously noticed, has smaller scattering than that indicated by latitude effect.

The twelve months' term has an amplitude C_1 lying between 5° for Peterhead and Carnsore and 16° for Prawle. The lines of equal amplitude are similar to the corresponding lines for annual variation of direction of arrival. The phase angles X_1 for this term lie between 0° and 62° , or between 42° and 62° if Carnsore be omitted, the corresponding dates of

maximum standard deviation being August 2nd for Lizard and July 13th for Browhead. Lines of equal phase may also nearly coincide with the lines of equal amplitude: the data are insufficient to decide.

The six months' term has an amplitude C_2 averaging $2/3$ of C_1 , (which is itself about $1/3$ of C_0). This term has a somewhat smaller amplitude in lower latitudes than in higher. The phase angles and higher harmonics have no features of special interest.

The standard deviation from the most frequent direction of arrival has, then, a mean value for the country of 28° , with a variation of twelve months' period giving a maximum standard deviation a month after the summer solstice, this variation having a total range of 18° . The term of six months' period is of some importance, it has a range of 12° and a maximum slightly earlier than that of the annual term. The mean standard deviation in the lower latitudes is about twice that in higher, the annual variation is greater in the S.E. than in the N.W.

IX. *Conclusion.*

The salient features of the statistical reduction may conveniently be collected here for reference.

The Diurnal Variation of Direction of Arrival has a range of some 35° , a counter-clockwise swing of that amount taking place between the midnight to sunrise period and the noon-sunset period. This diurnal range decreases with increasing latitude, from 58° at Lizard to 22° at Peterhead. The mean is displaced counter-clockwise from the mode at all times save between noon and sunset, and most so between sunset and midnight.

The scattering from the most frequently disturbed direction is generally less in higher latitudes, greatest in sunrise-noon and least in sunset-midnight period.

Observations made during daylight give a mean displaced counter-clockwise by 26° from the mean for dark hour observations. The scattering in daylight is 50 per cent. greater than in the dark.

Observations made before noon are displaced 15° clockwise from those made after noon. The mean of observations after noon is displaced 6° counter-clockwise from the corresponding mode. The scattering before noon is 20 per cent. greater than after noon.

The Seasonal Variation takes a form which, when referred to solar altitude, is similar to the Diurnal. A counter-clockwise swing of some 30° takes place from Spring to Summer.

The mean is displaced clockwise from the mode in Summer and low latitudes, counter-clockwise in Winter and high latitudes. The scattering from the most frequently disturbed direction is least in Spring, greatest in Summer, and is generally less in high latitudes.

The general mean directions of arrival are readily visualized as crossing the island of Majorca.

The mean curves of monthly mean and monthly most frequent directions of disturbance are adequately represented by the expression.

$$X = 138 + 20 \sin (\phi + 230) + 8 \sin 2(\phi + 90),$$

where ϕ is a date measured in days from June 15th.

The scattering from these monthly values is such that some 70 per cent. of all observations will fall within a range of $X_F \pm \sigma_F$ where $\sigma_F = 28^\circ + 9 \sin (\phi + 50) + 6 \sin 2(\phi + 50)$.

The annual variation of direction is large in the S.E., small in the N.W., the maximum deviations from the mean occur earlier in the W., later in the E., and on the mean about a month after the solstices. The semi-annual variation follows a similar law of phase variation with longitude.

The scattering also reaches a maximum about one month after the summer solstice, the mean scattering in lower latitudes is twice that of higher latitudes, and the annual variation of scattering is greater in the S.E. than in the N.W.

It is somewhat unfortunate that the group of stations giving reports sufficiently numerous for full analysis does not include a station in the S.E. of England, to verify these conclusions. Lydd ($50^\circ 58' 20''$ N., $0^\circ 53' 50''$ E.) is well situated, and while its total number of observations reaches only 594, it has been thought worth while to make a partial analysis to test the conclusions that a South-Easterly location favours large annual range, late incidence of annual and semi-annual maxima, large standard deviation, and large annual range of standard deviation.

The results are, considering the paucity of observations, satisfactory. The analysis of monthly mean directions of arrival at Lydd gives a C_0 term of 112° , a C_1 of 70° , an X_1 of 218° , and X_2 of 71° . Thus the annual range is nearly double that of the next station analysed, the annual term has a phase less than 10° (or ten days) out of agreement with the longitude law, the phase of the semi-annual term is in complete agreement with the law. The standard deviations for Lydd give a C_0 term of 38° , C_1 15° , X_1 75° , and X_2 89° . These fit in well with the main results, as they show this

South-Easterly station to have the largest mean standard deviation of all, and an annual range of standard deviation only 1° less than the maximum (that of Prawle).

It would be rash to pursue much further, in face of the obvious limitations of the methods used and of the temporal distribution of the data, the implications of these results. It is sufficient in the present state of our knowledge, to have established in this and the preceding paper *, the essential regularity and simplicity of the general laws emerging from straightforward analysis of data obtained, near the two extremes of the gamut of practical radio frequencies, by standard direction-finding methods. The results themselves must, and must soon, be fitted into a geophysical theory, but their immediate value may rather lie in the encouragement which they offer to the worker seeking order in the superficial disorder of the incidence of naturally occurring electromagnetic waves.

Thanks are due to the Admiralty for the supply of the data and for permission to make use of them in publication, to the Meteorological Office and the Radio Research Board, under whose auspices the work was carried on, to Captain C. J. P. Cave, R.E., and Captain J. A. Slee, R.N., the officers responsible for the inception of the reporting system, and to Mrs. R. A. Watson Watt, who has carried out much the greater part of the reduction of data.

July 3, 1922.

ABSTRACT.

13,000 bearings of atmospherics, taken between 1916 and 1920, at six British coastal direction-finding stations, spread over $7\frac{1}{2}^\circ$ in latitude and 9° in longitude, are analysed statistically.

Diurnal and seasonal variations of the apparent direction of arrival of atmospherics are established, the sense of both variations being counter-clockwise with increasing solar altitude. The mean direction of arrival is about 140° E. of N., the mean diurnal range and mean seasonal range are both of the order of 30° , both ranges decrease with increasing latitude. The distribution is skew, the mean being displaced clockwise from the mode (1) in the afternoon, (2) in summer, and (3) in low latitudes, counter-clockwise (1) at other times of the day, (2) in winter, and (3) in high latitudes.

Observations in daylight give a mean displaced 26° counter-clockwise from the mean for dark hour observations. Observations between noon and midnight have a mean 15° counter-clockwise from that for

* *Loc. cit.*

observations between midnight and noon. "P.M." observations show particularly marked skewness, evidently due to the sunset midnight period.

The scattering from the mean or mode for the group, measured by the standard deviation, is great (1) between sunrise and noon, (2) in daylight, (3) A.M., (4) in summer, (5) in low latitudes and small, (1) between sunset and midnight, (2) in darkness, (3) P.M., (4) in spring, (5) in high latitudes.

Fourier analysis of monthly means and modes gives non-periodic terms between 130° and 150° , variations of twelve-monthly period with amplitudes between 4° and 40° , this amplitude being great in the S.E., small in the N.W., the maximum deviation from mean occurring early in the W., late in the E., and on the mean about one month after the solstices. The variation of six-monthly period follows a similar longitude-phase law.

The scattering reaches its maximum about one month after the summer solstice, is less in high latitudes, and its annual range is greater in the S.E. than in the N.W.

These results are tested in the case of a seventh station in S.E. England.

CIII. *The Calculation of the Skin Effect in Electrical Conductors.* By F. F. P. BISACRE, O.B.E., M.A., A.M.Inst.C.E.*

IT is well known that the calculation of the skin effect in straight cylindrical conductors, carrying alternating currents, can be made by means of Bessel Functions of argument $+\sqrt{-j}x$, where $j = +\sqrt{-1}$.

It is usual to split up the required functions into real and imaginary parts, thus:

$$J_0(\sqrt{-j}x) = \text{ber } x + j \text{ bei } x = I_0(\sqrt{j}x), \quad \dots \quad (1)$$

$$\frac{d}{dx} J_0(\sqrt{-j}x) = \text{ber}' x + j \text{bei}' x = \frac{d}{dx} I_0(\sqrt{j}x), \quad \dots \quad (2)$$

$$K_0(\sqrt{j}x) = \text{ker } x + j \text{kei } x, \quad \dots \quad (3)$$

$$\frac{d}{dx} K_0(\sqrt{j}x) = \text{ker}' x + j \text{kei}' x, \quad \dots \quad (4)$$

Eight functions therefore enter the general calculation †.

Some years ago the writer had occasion to make calculations of the skin effect in some rather complicated cases.

* Communicated by Sir J. J. Thomson, O.M., F.R.S.

† Russell, Phil. Mag. April 1909, and 'Alternating Currents,' vol. i. p. 207 (1914 Ed.).

He found, as he thought, that there were several objections to the above "ber-bei" method.

1. There are no less than eight functions to handle, to say nothing of the combinations of these; the algebra is consequently very heavy, as Heaviside and Russell have observed.

2. The beauty of the complex variable * seems to be lost if the functions are split up in this way.

3. The symbols for these functions are cumbrous to write, and unless the writing is good, $\text{ber}'x$ degenerates into $\text{bei}x$, $\text{ker}'x$ into $\text{kei}x$, and so on!

Professor Kennelly has published tables for $J_0(\sqrt{-j}x)$ and $J_1(\sqrt{-j}x)$ in his vector notation †, and these are simple to use, but they are applicable only to the solid straight conductor, and the results for this case have been tabulated by Pedersen ‡.

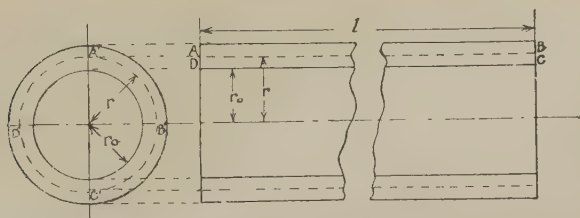
The problem of the single, solid, straight conductor seems, therefore, to have been completely solved. The problems of the straight, tubular conductor and the straight, concentric cable remain.

The author proposes to discuss a method which is readily applicable to these problems and is simple in its numerical use.

Differential Equations.

Let μ be the permeability of the material of the wire, ρ the specific resistance, i the current density at radius r

Fig. 1.



(fig. 1), h the tangential magnetic-field strength at radius r . We assume that the magnetic flux surrounds the wire in circles, the planes of which are perpendicular to the axis of

* As used, for instance, by Sir J. J. Thomson in 'Recent Researches in Electricity and Magnetism' (1893 Ed.; p. 262 *et seq.*).

† Amer. Inst. of Electrical Engineers, vol. xxxiv. no. 8, p. 1795.

‡ *Jahrbuch der Drahtlosen Telegraphie und Telephonie*, vol. iv. pp. 501-515.

the wire and the centres on the axis, and that equipotential surfaces are planes perpendicular to the axis—*i. e.*, the radial current in the wire is ignored.

By applying Faraday's Law of Electromagnetic Induction to the circuit A B C D (fig. 1), we get

$$\rho(i - i_0)l = \frac{\partial}{\partial t} \left[\mu l \int_{r_0}^r h dr \right].$$

$$\therefore \quad \rho \frac{\partial i}{\partial r} = \mu \frac{\partial h}{\partial t} \quad \dots \dots \dots (A)$$

Similarly, by applying the law that the line-integral of the magnetic force round a circuit equals 4π times the current enclosed, we get for A' B' C' D',

$$r h = 4\pi \int_{r_0}^r i r dr.$$

$$\therefore \quad \frac{1}{r} \frac{\partial}{\partial r} (r h) = 4\pi i \quad \dots \dots \dots (B)$$

Equations (A) and (B) are the fundamental differential equations. We can eliminate h or i from these two equations, getting

$$\frac{\partial^2 i}{\partial r^2} + \frac{1}{r} \frac{\partial i}{\partial r} = \frac{4\pi\mu}{\rho} \frac{\partial i}{\partial t} \quad \dots \dots \dots (5)$$

$$\text{and} \quad \frac{\partial^2 h}{\partial r^2} + \frac{1}{r} \frac{\partial h}{\partial r} - \frac{h}{r^2} = \frac{4\pi\mu}{\rho} \frac{\partial h}{\partial t} \quad \dots \dots \dots (6)$$

These equations apply in the material of the wire.

The words "magnetic force" and "current" are used in a generalized sense in the following analysis for any functions that satisfy equations (A) and (B) whether the functions be real or complex. The conditions of a particular problem are then specified just as if these quantities were magnetic forces and currents in a physical sense. The "generalized pressure" follows from equation (19) derived in this way. It is well known—and can be easily proved—that if equations (5) and (6) are solved in complex functions and the solution fitted to the generalized conditions of any special problem, then either the real part or the imaginary part of the solution gives a physical solution corresponding to a real current, magnetic force, and electrical pressure.

*General Solution of the Differential Equation
for Current.*

If i is a sinusoidal function of time, we may assume that i is of the form $Se^{j\omega t}$, where S is a complex function of r only to be determined and $\omega = 2\pi n$, where n is the frequency.

Substituting this value of i in equation (5), we get

$$\frac{d^2S}{dr^2} + \frac{1}{r} \frac{dS}{dr} + k^2 S = 0, \quad \dots \dots \dots (7)$$

where

$$k^2 = -j \frac{4\pi\mu\omega}{\rho} \dots \dots \dots (8)$$

Put

$$q^2 = \frac{4\pi\mu\omega}{\rho}, \quad \dots \dots \dots (9)$$

then

$$k = \sqrt{-j} q, \quad \dots \dots \dots (10)$$

where q is a real number.

The solution of equation (7) is

$$S = c_1 J_0(kr) + c_2 H_0(kr), \quad \dots \dots \dots (11)$$

where $J_0(kr)$ is the Bessel function of the first kind, of zeroth order, and $H_0(kr)$ is a Bessel function of the second kind, of zeroth order.

The complete expression for i runs

$$i = [c_1 J_0(kr) + c_2 H_0(kr)] e^{j\omega t}, \quad \dots \dots \dots (12)$$

where c_1 and c_2 are constants to be found from the conditions of the problem.

Since $\rho \frac{\partial i}{\partial r} = \mu \frac{\partial h}{\partial t}$, we easily get (remembering that $\frac{d}{dx} \cdot J_0(x) = -J_1(x)$),

$$h = \frac{4\pi}{k} [c_1 J_1(kr) + c_2 H_1(kr)] e^{j\omega t} \dots \dots \dots (13)$$

Equations (12) and (13) involve two constants only, to be determined.

By equation (10), we have

$$k = +\sqrt{-j} q, \text{ the +ve sign by definition,} \\ = q(\cos 45^\circ - j \sin 45^\circ);$$

$$i. e. \dots k = [q, -45^\circ], \dots \dots \dots (14)$$

and $kr = [qr, -45^\circ]$, where qr is a real number.

$[qr, -45^\circ]$ is sometimes written $qr \overline{45^\circ}$, a vector of length qr , turned through an angle, -45° , relative to the initial line. This notation seems to have no real advantage over $[qr, -45^\circ]$, and it is more difficult and expensive to print.

The Hankel Functions.

The H functions (*Funktionentafeln*, p. 94) * are used instead of the K or G, as H seems to be the symbol for Bessel functions of the second kind for complex arguments which has not been defined by mathematicians in several different ways †.

There are two Hankel functions, the choice between which depends on whether the imaginary part of the argument is positive or negative. If the imaginary part of z is positive, we use $H_p^{(1)}(z)$, defined by

$$j\frac{\pi}{2}H_p^{(1)}(z) = \alpha J_p(z) - Y_p(z) + j\frac{\pi}{2}J_p(z), \quad . \quad . \quad (15)$$

where $\alpha = (\log 2 - \gamma)$, γ is Euler's constant, and $Y_p(z)$ is the usual Neumann function ‡.

If the imaginary part of z is negative, we use $H_p^{(2)}(z)$, defined by :

$$-j\frac{\pi}{2}H_p^{(2)}(z) = \alpha J_p(z) - Y_p(z) - j\frac{\pi}{2}J_p(z). \quad . \quad (16)$$

The function $H_p^{(1)}(z)$ is used for $z = re^{j\theta}$, $0 < \theta < \pi$, the second, $H_p^{(2)}(z)$, for $z = re^{-j\theta}$, $0 < \theta < \pi$.

In the usual ker-kei notation, we get

$$-j\frac{\pi}{2}H_0^{(2)}(\sqrt{-j} \cdot x) = \ker x + j \operatorname{kei} x. \quad . \quad . \quad (17)$$

The ker-kei notation is employed in the B. A. Tables (1915) and in Russell's 'Alternating Currents,' vol. i. p. 209. The H functions approach zero as the modulus of the argument approaches infinity.

* Jahnke & Emde, '*Funktionentafeln mit Formeln und Kurven*.' Teubner, 1909.

† The theory of these functions is no concern of the applied physicist—it is sufficient for his purpose if he knows their properties and where he can get tables of their values. "The choice of a standard solution" of the second kind "is largely a matter of convention, since the differential equation is still satisfied if we add any constant multiple of $J_n(x)$ " (Lamb, '*Hydrodynamics*').

There are some 16 different "standard" solutions, and unfortunately the same letter has often been used in different senses. The relations of the different notations are set out in a table (p. 173, Jahnke & Emde, '*Funktionentafeln*').

‡ Defined p. 93, Jahnke & Emde, '*Funktionentafeln*'.

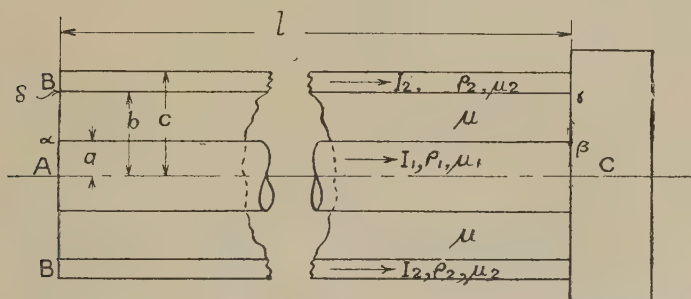
We are only concerned with the $H_p^{(2)}(z)$ function as the imaginary part of the argument is negative; hence we shall write $H_p(z)$ for $H_p^{(2)}(z)$.

The Concentric Cable.

We shall now deal with the problem of the concentric cable.

Suppose (fig. 2) the outer conductor is composed of material of specific resistance ρ_2 and permeability μ_2 , the inner, of specific resistance ρ_1 and permeability μ_1^* , and let μ be the permeability of the material occupying the insulation space.

Fig. 2.



Let I_1 be the total current flowing in the inner at any instant, eastwards, and I_2 the total current in the outer at the same instant eastwards, then $I_1 + I_2 = 0$.

The conditions of potential are that the potential *all over* the end A is constant; all over the end B, constant; and over the short-circuited end C, constant; hence the pressure-drop between A and B is that in the filamental circuit $\alpha\beta + \gamma\delta$. The drop is clearly $l[\rho_1 i_a + \text{drop required to overcome the inductive e.m.f. due to the flux in the insulation space} - \rho_2 i_b]$, the last term having the negative sign because i_b is the current from left to right.

$$\therefore V = l[\rho_1 i_a - \rho_2 i_b + \text{inductive e.m.f. due to insulation-flux}] \quad (18)$$

* The distinction is made mathematically between the properties of the material of the two conductors; but physical facts would have to be taken into account if these properties differed greatly, *e. g.* hysteresis losses, heat-conduction.

When $a < r < b$, $h = \frac{2I_1}{r}$, hence the total flux in the insulation-space is given by

$$\phi = \mu l \int_a^b \frac{2I_1}{r} dr = 2I_1 \mu l \log \frac{b}{a}.$$

$$\therefore V = l \left[\rho_1 i_a - \rho_2 i_b + 2\dot{I}_1 \mu \log \frac{b}{a} \right]. \quad (19)$$

Now $\rho \frac{\partial i}{\partial r} = \mu \frac{\partial h}{\partial t}.$

$$\therefore \frac{\rho_2}{\mu_2} \left(\frac{\partial i}{\partial r} \right)_b = \left(\frac{\partial h}{\partial t} \right)_b = \frac{\partial}{\partial t} \left(\frac{2I_1}{b} \right) = \frac{2}{b} \frac{\partial I_1}{\partial t}.$$

Similarly

$$\frac{\rho_1}{\mu_1} \left(\frac{\partial i}{\partial r} \right)_a = \frac{2}{a} \frac{\partial I_1}{\partial t}.$$

$$\therefore V = 2l\dot{I}_1 \left[\frac{\mu_1 i_a}{a \left(\frac{\partial i}{\partial r} \right)_a} - \frac{\mu_2 i_b}{b \left(\frac{\partial i}{\partial r} \right)_b} + \mu \log \frac{b}{a} \right]. \quad (20)$$

The drop of pressure in the outer is clearly $(-\rho_2 i_c)l$ as there is no flux external to $r=c$; hence, to find the drop in the inner only, we merely have to subtract $(-\rho_2 i_c)l$; hence the pressure-drop along the inner, V_i , is given by

$$V_i = l \left[\rho_1 i_a + \rho_2 (i_c - i_b) + 2\dot{I}_1 \mu \log \frac{b}{a} \right], \quad (21)$$

and that along outer conductor, V_o , by

$$V_o = -\rho_2 i_c l, \quad (22)$$

giving a total drop, V , of the value stated in equation (19).

This analysis holds, whatever function I_1 may be of time or whatever the distribution of current may be.

To find expressions for the equivalent resistance and reactance for alternating currents, we need a formula for i , the current density, which may be obtained thus:—

The magnetic conditions are :

$$h = \frac{2I_1}{a} \quad \text{at } r=a,$$

$$\frac{2I_1}{b} \quad \text{at } r=b,$$

$$0 \quad \text{at } r=c \text{ and } r>c.$$

By equation (13), if $I_1 = I_1' e^{j\omega t}$, where I_1' may be a complex number, we get, for the inner conductor,

$$\frac{2I_1' e^{j\omega t}}{a} = \frac{4\pi}{k} [c_1 J_1(ka)] e^{j\omega t},$$

since h is finite at $r=0$ and $\lim_{r \rightarrow 0} |H_1(kr)| = \infty$.

$$\therefore c_1 = \frac{k_1}{4\pi} \cdot \frac{2I_1'}{a} \cdot \frac{1}{J_1(ka)}, \quad \dots \dots (22)'$$

where k_1 is the value of k for the material of the inner conductor.

Also
$$\left(\frac{\partial i}{\partial r} \right)_a = \frac{1}{k_1} \cdot \frac{J_0(k_1 a)}{J_0'(k_1 a)}, \text{ by equation (12),}$$

where
$$k_1 = \sqrt{-j} \cdot \sqrt{\frac{4\pi\mu_1\omega}{\rho_1}}.$$

Similarly, for the outer conductor

$$\frac{2I_1'}{b} = \frac{4\pi}{k_2} [c_1 J_1(k_2 b) + c_2 H_1(k_2 b)], \text{ by equation (13),}$$

and
$$0 = \frac{4\pi}{k_2} [c_1 J_1(k_2 c) + c_2 H_1(k_2 c)],$$

where
$$k_2 = \sqrt{-j} \cdot \sqrt{\frac{4\pi\mu_2\omega}{\rho_2}}.$$

We now define a function of $k_2 r$ in the following way:—

Put
$$\Delta_n(k_2 r, k_2 c) = \left\{ \begin{array}{l} J_n(k_2 r), H_n(k_2 r) \\ J_1(k_2 c), H_1(k_2 c) \end{array} \right\}, \text{ } n \text{ being 0 or } \left. \begin{array}{l} \text{an integer.} \end{array} \right\} \quad (23)$$

We shall only need this function for $n=0$ and $n=1$.

Then
$$h = \frac{2I_1'}{b} \cdot \frac{\Delta_1(kr, kc)}{\Delta_1(kb, kc)} e^{j\omega t},$$

for this expression is of the form (13) above and gives the correct values of h when $r=b$ and $r=c$ —and, by equations (12) and (13),

$$\begin{aligned} i &= \frac{k_2}{4\pi} \cdot \frac{2I_1'}{b} \cdot \frac{\Delta_0(kr, kc)}{\Delta_1(kb, kc)} e^{j\omega t}, \\ &= \frac{k_2 I_1'}{2\pi b} \cdot \frac{\Delta_0(kr, kc)}{\Delta_1(kb, kc)} e^{j\omega t} \dots \dots \dots (24) \end{aligned}$$

Also $\frac{d\Delta_0}{dr} = k_2\Delta_0'$, where $\Delta_0'(x)$ is $\frac{d}{dx}\Delta_0(x)$,

hence
$$\frac{i_b}{\left(\frac{\partial i}{\partial r}\right)_b} = \frac{1}{k_2} \frac{\Delta_0(k_2b, k_2c)}{\Delta_0'(k_2b, k_2c)}.$$

Substituting now in (20), we get

$$V = 2I_1 \left[\frac{\mu_1}{k_1a} \frac{J_0(k_1a)}{J_0'(k_1a)} - \frac{\mu_2}{k_2b} \frac{\Delta_0(k_2b, k_2c)}{\Delta_0'(k_2b, k_2c)} + \mu \log \frac{b}{a} \right]. \quad (25)$$

But $\dot{I}_1 = I_1' j\omega e^{j\omega t}$.

$$\therefore V = I_1' e^{j\omega t} \left[-\frac{2lj\omega\mu_1}{k_1a} \frac{J_0(k_1a)}{J_1(k_1a)} + \frac{2lj\omega\mu_2}{k_2b} \frac{\Delta_0(k_2b, k_2c)}{\Delta_1(k_2b, k_2c)} + 2lj\omega\mu \log \frac{b}{a} \right], \quad (26)$$

in which accented Bessel Functions are replaced by functions of the first order, with sign changed.

The quantity in [] can be put in the form $\alpha + j\omega\beta$, where α and β are, by definition, *real* numbers.

What is the physical significance of these numbers? We know that

$$\begin{aligned} V &= (\alpha + j\omega\beta) I_1' e^{j\omega t} \\ &= \alpha I_1 + \beta \frac{\partial I_1}{\partial t}, \end{aligned}$$

on replacing $I_1' e^{j\omega t}$ by I_1 .

V and I_1 are both complex numbers, representing pressure and current. Let

$$V = V_1 + jV_2,$$

$$I_1 = C_1 + jC_2.$$

On substituting and equating real and imaginary parts, we get

$$V_1 = \alpha C_1 + \beta \frac{\partial C_1}{\partial t},$$

$$V_2 = \alpha C_2 + \beta \frac{\partial C_2}{\partial t}.$$

By the principle mentioned on page 1028, either of these equations gives a real solution of the problem, *i. e.*, a physical

current corresponding to a physical pressure; but either of these equations is exactly the same equation as we should have connecting an e.m.f. and a current in an inductive circuit of resistance α and inductance β ,

$$\therefore \quad \alpha + j\omega\beta = R + j\omega L,$$

where R is the equivalent resistance and L the equivalent self-inductance, *i. e.*

$$R + j\omega L = 2j\omega \left[-\frac{\mu_1}{k_1 a} \frac{J_0(k_1 a)}{J_1(k_1 a)} + \frac{\mu_2}{k_2 b} \frac{\Delta_0(k_2 b, k_2 c)}{\Delta_1(k_2 b, k_2 c)} + \mu \log \frac{b}{a} \right]. \quad (27)$$

This result is the *accurate* solution of the problem of the complete concentric circuit.

The further analysis of this result is facilitated by study of the Δ functions.

Δ Functions.

The Δ function is straightforward to handle analytically, and, what is even more important in applied physics, it is convenient for numerical calculation and leads to systematic formulæ (*e. g.* equation (27) above).

Numerical Calculation of Δ 's.

For cases in which the argument has intermediate values—values too large for the “small”-value approximations and too small for the asymptotic ones, the Δ 's must be calculated from tables of the Bessel Functions concerned.

Tables for the following functions are given in $[r, \theta]$ and $[a + jb]$ form :

$$J_0(\sqrt{-j}x), J_1(\sqrt{-j}x), H_0(\sqrt{-j}x), H_1(\sqrt{-j}x).$$

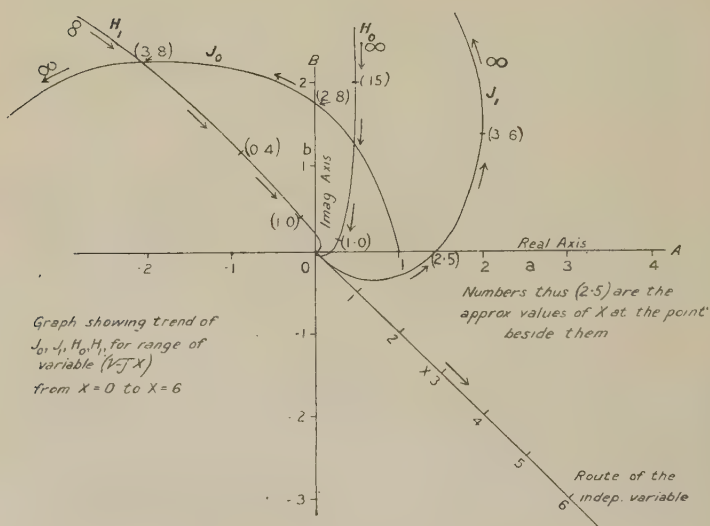
The tables for the J 's in the $[r, \theta]$ form have been calculated from the corresponding tables in the $(a + jb)$ form, due to St. Aldis (Proc. Roy. Soc. Lond. lxvi. pp. 42, 43, 1900). Kennelly also gives a table (Proc. Amer. Inst. Elect. Eng. xxxiv. no. 8, p. 1795) with which this table agrees very closely *. Tables for H_0 and H_1 in the $(a + jb)$ form are due

* The fundamental St. Aldis tables are reprinted in *Funktionentafeln* on pp. 137, 138. In these tables there is an error of sign in the imaginary part from $x=5.1$ to $x=6.0$ inclusive.

to Jahnke and Emde, from *Funktionentafeln*, pp. 139, 140; while the $[r, \theta]$ form has been computed from these values*.

The graph (fig. 3) shows the general trend of these functions. The accurate values of Δ_0 and Δ_1 can be computed from these values of the Bessel Functions, for the range $x=0$ to $x=6$. Above $x=6$ asymptotic expressions are available for the direct calculation of the functions required, viz. J_0/J_1 and Δ_0/Δ_1 —and nearly all practical cases are

Fig. 3.



covered by the asymptotic expressions, since the problem of "skin-effect" only becomes of practical importance in "wireless" work where the frequency is high. For this reason, it has not been thought worth while to give approximate formulæ for cases where the variable is small—for such cases, Tables I. and II. are available, while approximate formulæ can be very easily obtained from the series for the Bessel Functions.

* Miss M. M. Fleming and Mr. C. F. Powell have kindly checked these tables independently.

TABLE I.

$x.$	$J_0(\sqrt{-j}x)=[\rho, \theta]=(a+jb).$				$J_1(\sqrt{-j}x)=[\rho, \theta]=(a+jb).$			
	$\rho.$	$\theta.$	$a.$	$b.$	$\rho.$	$\theta.$	$a.$	$b.$
0.0	1.0000	0 0 0	+1.0000	+0.0000	0.0000	0 0 0	+0.0000	-0.0000
0.2	1.0001	0 34 23	+1.0000	+0.0100	0.1000	-44 42 59	+0.07106	-0.07036
0.4	1.0003	2 17 29	+0.9996	+0.0400	0.2000	-43 51 56	+0.1442	-0.1386
0.6	1.0020	5 9 11	+0.9980	+0.0900	0.3000	-42 25 12	+0.2215	-0.2024
0.8	1.0064	9 8 32	+0.9936	+0.1599	0.4004	-40 25 16	+0.3048	-0.2596
1.0	1.0158	14 13 13	+0.9844	+0.2496	0.5013	-37 51 11	+0.3958	-0.3076
1.2	1.0319	20 20 26	+0.9676	+0.3587	0.6032	-34 42 6	+0.4959	-0.3434
1.4	1.0586	27 22 13	+0.9401	+0.4867	0.7069	-31 0 35	+0.6059	-0.3642
1.6	1.0984	35 10 13	+0.8979	+0.6327	0.8136	-26 46 0	+0.7264	-0.3664
1.8	1.1544	43 32 49	+0.8367	+0.7953	0.9244	-22 0 2	+0.8571	-0.3463
2.0	1.2291	52 17 31	+0.7517	+0.9723	1.0412	-16 43 45	+0.9971	-0.2997
2.2	1.3247	61 13 2	+0.6377	+1.1610	1.1634	-11 1 33	+1.1419	-0.2225
2.4	1.4429	70 11 24	+0.4890	+1.3575	1.3012	-4 50 10	+1.2966	-0.1097
2.6	1.5856	79 5 23	+0.3001	+1.5569	1.4498	+1 42 7	+1.4491	+0.04306
2.8	1.7541	87 52 23	+0.0651	+1.7529	1.6148	8 34 7	+1.5968	+0.2406
3.0	1.9502	96 31 7	-0.2214	+1.9376	1.7998	15 42 54	+1.7326	+0.4875
3.2	2.1761	105 1 57	-0.5644	+2.1916	2.0088	23 4 50	+1.8480	+0.7875
3.4	2.4342	113 25 58	-0.9680	+2.2334	2.2459	30 37 19	+1.9327	+1.1440
3.6	2.7282	121 44 58	-1.4353	+2.3199	2.5155	38 17 45	+1.9742	+1.5.89
3.8	3.0613	129 59 28	-1.9674	+2.3454	2.8226	46 3 59	+1.9584	+2.0327
4.0	3.4391	138 11 26	-2.5634	+2.2927	3.1729	53 54 22	+1.8692	+2.5639
4.2	3.8671	146 21.39	-3.2195	+2.1422	3.5722	61 47 24	+1.6886	+3.1479
4.4	4.3518	154 30 47	-3.9283	+1.8726	4.0274	69 42 19	+1.3969	+3.7774
4.6	4.9012	162 39 26	-4.6784	+1.4610	4.5459	77 38 28	+0.9730	+4.4406
4.8	5.5243	170 47 42	-5.4531	+0.8837	5.1366	85 35 27	+0.3949	+5.1214
5.0	6.2313	178 56 0	-6.2301	+0.1160	5.8091	93 33 4	-0.3598	+5.7979
5.2	7.0338	187 4 14	-6.9803	-0.8658	6.5745	101 31 3	-1.3127	+6.4421
5.4	7.9453	195 12 36	-7.6674	-2.0845	7.4456	109 29 31	-2.4844	+7.0189
5.6	8.9821	203 20 52	-8.2466	-3.5597	8.4371	117 28 20	-3.8922	+7.4857
5.8	10.160	211 29 12	-8.6644	-5.3068	9.5510	125 31 18	-5.5492	+7.7735
6.0	11.501	219 37 30	-8.8583	-7.3347	10.850	133 27 8	-7.4622	+7.8767

Columns a & b are by H. Steadman Aldis (Proc. Roy. Soc. Lond. lvi. pp. 42, 43, 1900). Columns ρ & θ computed from a 's and b 's. The signs of the imaginary part in Jahnke & Emde's Table, p. 137, from 5.1 to 6.0, are as in their graph; not as in their Table.

Columns a & b are by H. Steadman Aldis (*loc. cit.*). His figures have been divided by $\sqrt{2}$. Columns ρ & θ computed from a 's & b 's.

TABLE II.

$x.$	$H_0^{(2)}(\sqrt{-j}x)=[\rho, \theta]=(a+jb).$				$H_1^{(2)}(\sqrt{-j}x)=[\rho, \theta]=(a+jb).$			
	$\rho.$	$\theta.$	$a.$	$b.$	$\rho.$	$\theta.$	$a.$	$b.$
0.0	∞	$\overset{\circ}{90} \overset{'}{0} \overset{''}{0}$	+0.5000	∞	∞	$\overset{\circ}{135} \overset{'}{0} \overset{''}{0}$	$-\infty$	$+\infty$
0.2	1.2042	66 22 29	+0.4826	+1.1033	3.1373	132 24 26	-2.1158	+2.316
0.4	0.8114	56 29 10	+0.4480	+0.6765	1.5103	127 30 12	-0.9195	+1.198
0.6	0.5995	47 23 59	+0.4058	+0.4413	0.9534	121 33 23	-0.4989	+0.812
0.8	0.4617	38 38 33	+0.3606	+0.2883	0.6688	115 0 59	-0.2828	+0.606
1.0	0.3641	30 4 43	+0.3151	+0.1825	0.4958	108 6 6	-0.1541	+0.471
1.2	0.2918	21 36 56	+0.2713	+0.1075	0.3801	100 56 2	-0.07210	+0.375
1.4	0.2366	13 14 36	+0.2303	+0.05420	0.2980	93 35 12	-0.01864	+0.297
1.6	0.1933	4 55 23	+0.1926	+0.01659	0.2373	86 6 27	+0.01611	+0.236
1.8	0.1591	- 3 21 54	+0.1588	-0.009338	0.1913	78 31 43	+0.03804	+0.187
2.0	0.1316	- 11 37 18	+0.1289	-0.02651	0.1555	70 52 17	+0.05096	+0.146
2.2	0.1091	- 19 53 23	+0.1026	-0.03712	0.1274	63 9 14	+0.05752	+0.113
2.4	0.09112	- 28 5 11	+0.08039	-0.04290	0.1049	55 23 12	+0.05960	+0.086
2.6	0.07587	- 36 1 49	+0.06136	-0.04463	0.08684	47 34 51	+0.05858	+0.064
2.8	0.06383	- 44 29 55	+0.04553	-0.04474	0.07216	39 44 11	+0.05549	+0.046
3.0	0.05367	- 52 39 14	+0.03256	-0.04267	0.06017	31 51 59	+0.05110	+0.031
3.2	0.04517	- 60 49 28	+0.02202	-0.03944	0.05032	23 59 8	+0.04598	+0.020
3.4	0.03810	- 68 59 30	+0.01366	-0.03557	0.04218	16 4 2	+0.04053	+0.011
3.6	0.03219	- 77 9 53	+0.007152	-0.03139	0.03537	8 9 5	+0.03509	+0.005
3.8	0.02514	- 85 16 23	+0.002154	-0.02605	0.02990	0 11 3	+0.02984	+0.000
4.0	0.02308	- 93 28 20	-0.001398	-0.02304	0.02517	- 7 46 36	+0.02493	-0.003
4.2	0.01957	-101 37 22	-0.003943	-0.01917	0.02126	-15 44 57	+0.02046	-0.005
4.4	0.01662	-109 45 54	-0.005620	-0.01564	0.01798	-23 43 53	+0.01646	-0.007
4.6	0.01412	-117 54 2	-0.006608	-0.01248	0.01523	-31 43 23	+0.01295	-0.008
4.8	0.01201	-126 2 37	-0.007066	-0.009710	0.01291	-39 42 37	+0.009932	-0.008
5.0	0.01021	-134 15 27	-0.007122	-0.007309	0.01096	-47 43 47	+0.007371	-0.008
5.2	0.008712	-142 19 10	-0.006893	-0.005325	0.009310	-55 44 31	+0.005241	-0.007
5.4	0.007422	-150 26 37	-0.006456	-0.003661	0.007917	-63 45 42	+0.003500	-0.007
5.6	0.006329	-158 34 30	-0.005892	-0.002312	0.006737	-71 47 9	+0.002106	-0.006
5.8	0.005402	-166 41 49	-0.005257	-0.001243	0.005738	-79 48 53	+0.001015	-0.005
6.0	0.004613	-174 49 6	-0.004594	-0.0004166	0.004890	-87 51 4	+0.0001834	-0.004
Columns a & b from Jahneke & Emde, p. 139, correcting the sign for the real part of $x=6.0$. Columns ρ & θ computed from a 's & b 's.					Columns a & b from Jahneke & Emde, p. 140, correcting the sign of the real part of $x=2.4$. Columns ρ & θ computed from a 's & b 's.			

Asymptotic Formulæ.

We require asymptotic formulæ for $\Delta_0(kr, kc)$ and $\Delta_1(kr, kc)$ and, in particular, the ratios

$$\frac{\Delta_0(kb, kc)}{\Delta_1(kb, kc)} \quad \text{and} \quad \frac{J_0(ka)}{J_1(ka)}.$$

Each of the latter can be obtained directly, without any knowledge of the asymptotic expansions of Bessel Functions, by a physical method*. Take the first one. The function we require an asymptotic expression for is a special value of

$$u_r = \frac{1}{k} \frac{\Delta_0(kr, kc)}{\Delta_1(kb, kc)}, \quad \text{viz. } u_b,$$

for then
$$\frac{\Delta_0(kb, kc)}{\Delta_1(kb, kc)} = k u_b.$$

This function, u_r , is clearly a solution of Bessel's Equation

$$\frac{d^2 u}{dr^2} + \frac{1}{r} \frac{du}{dr} + k^2 u = 0,$$

for it is of the type

$$A J_0(kr) + B H_0(kr),$$

and
$$\frac{du}{dr} = 0 \quad \text{when } r = c,$$

$$= -1 \quad \text{,, } r = b,$$

and
$$b \leq r \leq c.$$

Put $r = \frac{R}{q}$, and the equation becomes

$$\frac{d^2 u}{dR^2} + \frac{1}{R} \frac{du}{dR} + k_1^2 u = 0,$$

where
$$k_1 = \frac{k}{q}.$$

The conditions become

$$\frac{du}{dR} = 0 \quad \text{when } R = qc,$$

and
$$\frac{du}{dR} = -\frac{1}{q} \quad \text{when } R = qb,$$

and
$$qb \leq R \leq qc.$$

These conditions hold in the region between two concentric tubes of radii qb and qc , the radial gradient of u being

* Dr. J. Dougall suggested this method to the Author.

specified over the inner and outer tubes. Now, when q becomes large, the problem becomes that of finding u for a region between parallel plates, where surfaces of "equal u " are planes parallel to the boundary planes, and the specified radial derivatives become specified normal derivatives over the boundary planes.

Taking the origin in the westward boundary plane and x positive, eastward, we get

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + k_1^2 u = 0^*,$$

where $\frac{\partial^2 u}{\partial y^2} = 0$, to the first order.

$$\therefore \frac{\partial^2 u}{\partial x^2} + k_1^2 u = 0,$$

where $\frac{\partial u}{\partial x} = -\frac{1}{q}$, when $x=0$,

and $\frac{\partial u}{\partial x} = 0$, when $x=q(c-b)$,

whence
$$u = -\frac{1}{k_1 q} \frac{\cos k_1 \{q(c-b) - x\}}{\sin \{k_1 q(c-b)\}},$$

for this value of u clearly satisfies the conditions. Put $x=0$, and we get

$$\begin{aligned} u_b &= -\frac{1}{k_1 q} \cot k_1 q(c-b), \\ &= -\frac{1}{k} \cot k(c-b). \end{aligned} \quad (28)$$

The asymptotic value of $\frac{J_0(ka)}{J_1(ka)}$ can be similarly found, the solid cylinder becoming an infinite plane on the outside and the centre going to infinity, so that the equivalent "rectilinear" figure is a "half-space" bounded by an infinite plane.

If
$$u = \frac{1}{k} \frac{J_0(kr)}{J_1(ka)},$$

we get, asymptotically,

$$\frac{d^2 u}{dx^2} = \lambda^2 u, \text{ where } \lambda = j k_1,$$

* For full details of the transformation of this equation to the Bessel form, see Richardson, 'Electron Theory of Matter,' p. 26 *et seq.*

and $\frac{du}{dx} = \frac{1}{q}$ when $x=0$,
 $=0$ when $x \rightarrow \infty$;

i. e. $u = -\frac{1}{q\lambda} e^{-\lambda x},$

which gives, when $x=0$,
 $u_a = -\frac{1}{q\lambda};$

i. e. $\frac{1}{ka} \frac{J_0(ka)}{J_1(ka)} = \frac{j}{ka},$ asymptotically. (29)

The above method is not sufficiently refined to give the accurate asymptotic values of u_r itself for any value of r ; it merely gives the correct values at $r=b$ or $r=a$. The correct values can be found directly from the usual asymptotic formulæ for the Bessel Functions (*Funktionentafeln*, pp. 101, 102). The following values are at once obtained:—

$$\Delta_0(kr, kc) = \frac{2j}{\pi k \sqrt{rc}} \cos k(c-r), \quad (30)$$

$$\Delta_1(kr, kc) = -\frac{2j}{\pi k \sqrt{rc}} \sin k(c-r); \quad (31)$$

i. e. $\frac{\Delta_0(kr, kc)}{\Delta_1(kb, kc)} = -\sqrt{\frac{b}{r}} \frac{\cos k(c-r)}{\sin k(c-b)}, \quad (32)$

and $\frac{\Delta_0(kb, kc)}{\Delta_1(kb, kc)} = -\cot k(c-b) = -\frac{\sin \alpha + j \sinh \alpha}{\cosh \alpha - \cos \alpha},$

where $\alpha = \sqrt{2}q(c-b). \quad (33)$

At very high frequencies.

$$\left. \begin{aligned} \frac{\Delta_0(kb, kc)}{\Delta_1(kb, kc)} &= -j, \\ \frac{J_0(ka)}{J_1(ka)} &= +j. \end{aligned} \right\} (34)$$

while

Numerical Work.

The asymptotic expressions give simple formulæ for numerical work, bearing in mind that Kennelly has given a very useful table of functions of “semi-imaginaries” (see Table VI. of ‘Tables of Complex Hyperbolic and Circular

Functions': Kennelly)*. He gives values of \sinh , \cosh , \tanh , cosech , sech , and coth , where the argument is $[\rho, +45^\circ]$. The numbers are given in $[r, \theta]$ form. Transforming to hyperbolic functions of $[\rho, +45^\circ]$, we get:

$$\frac{\Delta_0(kb, kc)}{\Delta_1(kb, kc)} = -j \coth \{q(c-b), +45^\circ\}. \quad (35)$$

$$\Delta_0(kb, kc) = \frac{2j}{\pi k \sqrt{bc}} \cosh \{q(c-b), +45^\circ\}. \quad (36)$$

$$\Delta_1(kb, kc) = -\frac{2}{\pi k \sqrt{bc}} \sinh \{q(c-b), +45^\circ\}. \quad (37)$$

Combined Comparative Impedance.

By equation (27), we have

$$R + j\omega L = 2j\ell\omega \left[-\frac{\mu_1 J_0(ka)}{k_1 a J_1(ka)} + \frac{\mu_2 \Delta_0(k_2 b, k_2 c)}{k_2 b \Delta_1(k_2 b, k_2 c)} + \mu \log \frac{b}{a} \right]. \quad (38)$$

Now the areas of the cross-sections of the inner and outer conductors are usually equal, so that

$$a^2 = c^2 - b^2.$$

$$\therefore \frac{a}{c-b} = \frac{c+b}{a},$$

and b and c are each greater than a , therefore a is at least twice as great as $(c-b)$. Hence a higher order of approximation is required with the Δ_0/Δ_1 function than with J_0/J_1 .

We can therefore put

$$J_0/J_1 = j \text{ and } \Delta_0/\Delta_1 = -\cot k(c-b),$$

and R_n , the normal resistance of the whole circuit,

$$= \frac{\rho \ell}{\pi} \left[\frac{1}{a^2} + \frac{1}{c^2 - b^2} \right] = \frac{\rho \ell}{\pi} C. \quad (39)$$

Whence,

$$\frac{R + j\omega L}{R_n} = \frac{2\pi\omega}{\rho} \cdot \frac{1}{C} \cdot \left[\frac{\mu_1}{k_1 a} + \frac{\mu_2}{k_2 b} \coth \{q(c-b), 45^\circ\} + j\mu \log \frac{b}{a} \right], \quad (40)$$

where

$$C = \left[\frac{1}{a^2} + \frac{1}{c^2 - b^2} \right],$$

* The following formulæ are useful for transformations:—

$$\cos kx = \cosh (qx, +45^\circ),$$

$$\sin kx = -j \sinh (qx, +45^\circ),$$

$$\cot kx = j \coth (qx, +45^\circ).$$

The right-hand functions are all tabulated in Kennelly's tables, Table VI.

and the "coth" is given directly in Kennelly's Table. In the absence of this table

$$\cot k_2(c-b) = \frac{\sin \alpha + j \sinh \alpha}{\cosh \alpha - \cos \alpha}, \quad \dots \quad (41)$$

$$\text{where } \alpha = \sqrt{2}q_2(c-b) \text{ and } k_2(c-b) = \sqrt{-j}q_2(c-b). \quad (42)$$

Example. A concentric copper cable for which

$$a=0.75, \quad b=1, \quad c=1.25, \quad \rho_1=\rho_2=1700, \quad \mu_1=\mu_2=\mu=1.$$

Frequency 345. This relatively low frequency has been specially chosen to test the accuracy of the asymptotic formulæ for values of the variable well within the range of Tables I. & II.

$$q = \sqrt{\frac{4\pi\mu\omega}{\rho}} = 4.0.$$

$$C = 3.56 \text{ and}$$

$$\begin{aligned} \frac{R+j\omega L}{R_n} &= \frac{2\pi \times 345 \times 2\pi}{1700} \times \frac{1}{3.56} \times \left[\frac{1}{[3.0, -45^\circ]} \right. \\ &\quad \left. + \frac{[1.0746, -27^\circ 3']}{[4.0, -45^\circ]} + j 0.2877 \right] \\ &= 1.107 + j 1.360. \quad \dots \quad (43) \end{aligned}$$

$$\therefore \frac{R}{R_n} = 1.107, \quad \frac{X}{R_n} = 1.360, \text{ and } \frac{Z}{R_n} = 1.752, \quad \dots \quad (44)$$

Z being the equivalent impedance.

It is interesting to compare numerically the accurate and approximate values of J_0/J_1 and Δ_0/Δ_1 at this relatively low value of q .

$$\begin{aligned} J_0(3.00, -45^\circ) &= [1.0836, 80^\circ 48'] \text{ by Tables I. \& II.,} \\ J_1(3.00, -45^\circ) &= [1.0000, 90^\circ] \text{ by } +j \text{ approximation}^*. \end{aligned}$$

$$\begin{aligned} \frac{\Delta_0(4.00, -45^\circ; 5.00, -45^\circ)}{\Delta_1(4.00, -45^\circ; 5.00, -45^\circ)} &= -[0.9690, 64^\circ 53'] \\ &\quad \text{by Tables I. \& II.,} \\ &= -[1.0746, 62^\circ 57'] \\ &\quad \text{by } -\cot k_2(c-b), \\ &= -[1.0000, 90^\circ] \\ &\quad \text{by } -j \text{ approx.} \end{aligned}$$

* A closer approximation to $J_0(ka)/J_1(ka)$ is $j \left(1 - \frac{j}{2ka}\right)$.

The Heating of the Conductor.

Consider a coaxial tube of internal radius r and thickness δr , in the material of either conductor.

Let i_r be the complex current density in this tube.

Then, since the physical current is the real part of the current in the tube, $2\pi r\delta r \times i_r$, the heat generated in time δt in this tube is

$$\frac{\rho l}{2\pi r\delta r} \times (\text{real part of } i_r)^2 \times (2\pi r\delta r)^2 \times \delta t. \quad (45)$$

Hence the mean rate at which heat is generated is

$$\frac{\rho l \cdot 2\pi r \cdot \delta r}{T} \int_0^T (\text{real part of } i_r)^2 dt. \quad (46)$$

Now $\frac{1}{T} \int_0^T (\text{real part of } i_r)^2 dt$ is $\frac{|i_r|^2}{2}$ as it is the mean-square of an alternating current whose maximum value is $|i_r|$. Hence, if W_i is the total rate of heat generation in the inner conductor, we get

$$W_i = \rho_1 l \pi \int_0^a |i_r|^2 r dr, \quad (47)$$

and, for the outer conductor,

$$W_o = \rho_2 l \pi \int_b^c |i_r|^2 r dr. \quad (48)$$

Inner Conductor.

$$i_r = \frac{k_1}{2\pi a} \cdot \frac{J_0(k_1 r)}{J_1(k_1 a)} I_1' e^{i\omega t} \text{ by equation (22)',} \quad (49)$$

$$\text{whence} \quad W_i = \frac{\rho_1 l \bar{I}^2 q_1^2}{2\pi a^2} \int_0^a \left| \frac{J_0(k_1 r)}{J_1(k_1 a)} \right|^2 r dr, \quad (50)$$

where \bar{I} is the r.m.s. total current flowing.

$$\text{Now} \quad J_0(\sqrt{+j}x) J_0(\sqrt{-j}x) = |J_0(\sqrt{-j}x)|^2$$

because the factors on the left are conjugate complex numbers.

Also, we have the formula

$$\begin{aligned} (m^2 - n^2) \int_0^a r J_0(mr) J_0(nr) dr \\ = a \left[J_0(ma) \frac{\partial}{\partial a} J_0(na) - J_0(na) \frac{\partial}{\partial a} J_0(ma) \right]^*, \end{aligned} \quad (51)$$

* Pidduck, 'A Treatise on Electricity,' p. 13.

whence
$$\frac{W_i}{R_{n,i} \times \bar{I}^2} = \text{real part of } \frac{k_1 a}{2} \cdot \frac{J_0(k_1 a)}{J_1(k_1 a)}, \quad (52)$$

where $R_{n,i}$ is the normal resistance of the inner conductor.

(Tables for $\frac{ka}{2} \cdot \frac{J_0(ka)}{J_1(ka)}$ are given in Jahnke & Emde's *Funktionentafeln*, p. 147.)

Outer Conductor.

$$i_r = \frac{k_2}{2\pi b} \cdot \frac{\Delta_0(k_2 r, k_2 c)}{\Delta_1(k_2 b, k_2 c)} I_1' e^{j\omega t} \text{ by (24),}$$

whence
$$W_0 = \frac{\rho_2 l \bar{I}^2 q_2^2}{2\pi b^2} \int_b^c \left| \frac{\Delta_0(k_2 r, k_2 c)}{\Delta_1(k_2 b, k_2 c)} \right|^2 r dr. \quad (53)$$

(Compare with (50) above.)

With the help of theorem (51), which is a general one for all Bessel Functions, we can evaluate this integral if we wish, but it is hardly worth while, as the asymptotic formulæ give a very simple result, and it is only where these apply that the additional heating is appreciable.

We get

$$\frac{\Delta_0(k_2 r, k_2 c)}{\Delta_1(k_2 b, k_2 c)} = -\sqrt{\frac{b}{r}} \cdot \frac{\cos k_2(c-r)}{\sin k_2(c-b)}, \text{ by eq. (32),} \quad (54)$$

whence
$$\left| \frac{\Delta_0}{\Delta_1} \right|^2 r = b \cdot \frac{\cosh \phi + \cos \phi}{\cosh \alpha - \cos \alpha}, \quad (55)$$

where $\phi = \sqrt{2}q_2(c-r)$ and $\alpha = \sqrt{2}q_2(c-b)$.

Integrating, we get

$$W_0 = \frac{\rho_2 l \bar{I}^2 q_2^2}{2\sqrt{2}\pi b} \times \Phi,$$

where
$$\Phi = \frac{\sinh \alpha + \sin \alpha}{\cosh \alpha - \cos \alpha} \text{ and } \alpha = \sqrt{2}q_2(c-b). \quad (56)$$

Putting $R_{n,0}$ for the normal resistance of the outer conductor, we get

$$\frac{W_0}{R_{n,0} \bar{I}^2} = \frac{(c^2 - b^2)q_2}{2\sqrt{2}b} \times \Phi. \quad (57)$$

Whole Circuit.

If R_n is the normal resistance of the whole circuit, $R_n \bar{I}^2$ is the normal rate of heat-generation. The actual rate is

$(W_0 + W_i) = R\bar{I}^2$, where R is the equivalent heating resistance.

$$\therefore \frac{R}{R_n} = \frac{\text{actual rate of heat-generation}}{\text{normal rate of heat-generation}} = \frac{W_0 + W_i}{R_n \bar{I}^2},$$

whence, putting $C = \left[\frac{1}{a^2} + \frac{1}{c^2 - b^2} \right]$ as before, and assuming $\rho_1 = \rho_2$,

$$\frac{R}{R_n} = \frac{1}{C} \left[\text{real part of } \frac{k_1}{2a} \frac{J_0(k_1 a)}{J_1(k_1 a)} + \frac{g_2}{2\sqrt{2} \cdot b} \Phi \right]. \quad (58)$$

By comparing this expression with equation (40) for the equivalent impedance ratio of the whole circuit, it will be found, after a little reduction, that it is the real part of the equivalent impedance ratio, after putting $\frac{J_0(ka)}{J_1(ka)} = j$ as is done in deriving (40). The real part of the first term in (40) gives the energy loss ratio for the inner conductor; of the second term, for the outer; while the log. term is a pure reactance. It therefore seems natural to conclude that the first term in the total equivalent impedance ratio (40) belongs to the inner conductor, the second to the outer conductor, and the third to the inner, as a reactance. In a sense this is true, but it is not true, as we shall now show, that when so interpreted, the r.m.s. voltage across the outer conductor is $Z_0 \bar{I}$, where \bar{I} is the r.m.s. current flowing, and Z_0 the equivalent outer impedance so calculated.

As the frequency tends to infinity the pressure-drop across the outer conductor, and therefore the apparent equivalent impedance, tends to zero—not to infinity, as the second term in (40) does. It is evident that this is so from the fact that, as the frequency increases, the current in the outer conductor concentrates in the inner parts of it, and that $i_e \rightarrow 0$ as $q \rightarrow \infty$, as we shall presently show. There is no flux at all external to $r=c$; hence there can be no inductive e.m.f. on the outside of the outer conductor; and as the current-density on the outside tends to zero as the frequency increases, so, too, must the resistance drop, and hence the e.m.f. across the outer conductor.

The Outer Conductor and the Pressure across it.

$$i_e = \frac{k_2}{4\pi} \cdot \frac{2I_1'}{b} \cdot \frac{\Delta_0(k_2 c, k_2 c')}{\Delta_1(k_2 b, k_2 c)} e^{j\omega t}, \text{ by eq. (24).} \quad (59)$$

Now, by a theorem on linear differential equations of the second order*, we have

$$\Delta_0(k_2 c, k_2 c) = \frac{B}{k_2 c} \text{ where } B \text{ is constant.}$$

* Forsyth, 'Differential Equations,' 3rd ed. p. 181.

This equation is an accurate one; hence we can use the asymptotic expressions to find the value of B. We thus find

$$\Delta_0(k_2c, k_2c) = \frac{2j}{\pi k_2c} \dots \dots \dots (60)$$

If R_0 and L_0 are the *apparent* equivalent resistance and self-inductance of the outer conductor, we get, see (21),

$$(R_0 + j\omega L_0)I_1' e^{j\omega t} = -\rho_i c I,$$

whence
$$\frac{R_0 + j\omega L_0}{R_{n,0}} = \frac{c^2 - b^2}{\pi bc} \cdot \frac{1}{\Delta_1(k_2b, k_2c)} e^{-j\frac{\pi}{2}} \dots \dots (61)$$

This formula is an accurate one.

Putting *Asymptotic Formulae.*

$$\Delta_1(k_2b, k_2c) = -\frac{2}{\pi k\sqrt{bc}} \sinh \{q(c-b), 45^\circ\}, \text{ by eq. (31),}$$

we get

$$\frac{R_0 + j\omega L_0}{R_{n,0}} = \frac{(c^2 - b^2)q}{2\sqrt{bc}} \cdot e^{j\frac{\pi}{4}} \cdot \operatorname{cosech} \{q(c-b), 45^\circ\}, \quad (62)$$

where the cosech is tabulated in Kennelly's Tables.

Apparent Impedance of the Outer Conductor as $q \rightarrow \infty$.

The modulus of

$$\operatorname{cosech} \{q(c-b), 45^\circ\} \rightarrow 2e^{-\frac{q(c-b)}{\sqrt{2}}} \text{ as } q \rightarrow \infty,$$

and
$$q \cdot e^{-\frac{q(c-b)}{\sqrt{2}}} \rightarrow 0 \text{ as } q \rightarrow \infty.$$

$$\therefore \frac{R_0 + j\omega L_0}{R_{n,0}} \rightarrow 0 \text{ as } q \rightarrow \infty,$$

i. e. as the frequency increases, the whole pressure-drop across the outer and inner conductors, in series, tends to concentrate on the inner conductor—a result due to the fact that, while the outer conductor is under the magnetic influence of the inner, the inner is screened from the magnetic action of the outer conductor.

At very high frequencies, the formula for the relative apparent impedance becomes

$$\frac{R_0 + j\omega L_0}{R_{n,0}} = \frac{c^2 - b^2}{\sqrt{bc}} q e^{-\frac{q(c-b)}{\sqrt{2}}} e^{-j\left\{\frac{q(c-b)}{\sqrt{2}} - \frac{\pi}{4}\right\}} \dots \dots (63)$$

This result shows that, while the apparent impedance approaches zero with increasing frequency, the phase of the

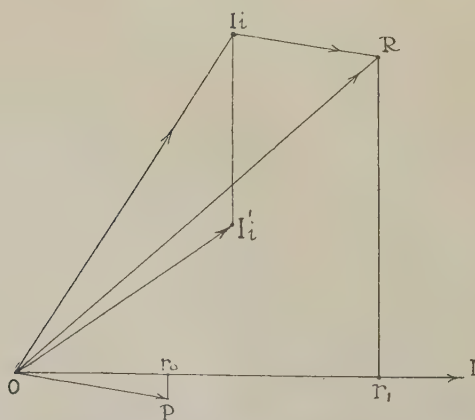
impedance vector decreases continuously with increasing frequency. As the frequency increases, the end of the apparent impedance vector rotating clockwise traces out a spiral of continually diminishing radius, and at certain frequencies the apparent resistance is negative—a somewhat curious result. This statement is true for large values of q for which the asymptotic expression is valid. The spiral begins on the real axis at $Z_0 = R_{n,0}$, and it can also be shown by expansion of the Bessel Functions in Δ_1 , in series of ascending powers of k as far as k^4 , that for *small values* of q the apparent resistance to alternating current is less than the normal resistance. It is therefore extremely probable—and numerical calculations confirm it—that for *all* values of q the apparent impedance vector is a decreasing one, beginning at value $R_{n,0}$ at $q=0$ and decreasing with increase of q ; the vector rotates clockwise so that the end of the apparent impedance vector describes a negatively-drawn spiral about the origin, beginning at the real point $(+R_{n,0})$ when $q=0$, and ending at the origin when $q \rightarrow \infty$.

Vector diagrams.

A typical vector diagram is given in fig. 4. It is drawn for the case of a concentric copper cable, for which

$$\begin{aligned} a &= 0.75 \text{ cm.} & \mu_1 &= \mu_2 = \mu = 1. \\ b &= 1.00 \text{ ,,} & \rho_2 &= \rho_1 = 1700. \\ c &= 1.25 \text{ ,,} & \sim &= 345. \\ R_{n,0} = R_{n,i} &= 1 \text{ ohm.} & q &= 4. \end{aligned}$$

Fig. 4.



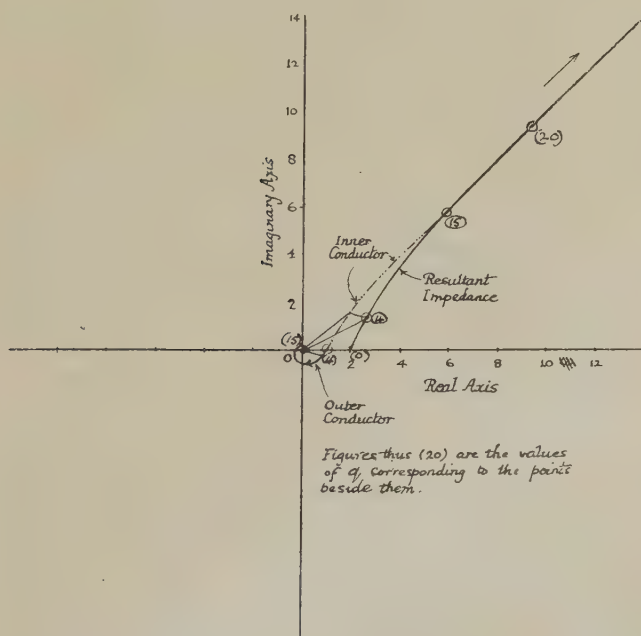
Vector Diagram, showing pressure and current for concentric main.

Description of Pressure Vectors.

- OI, current vector.
- OI_1 , in-phase resistance drop in whole circuit.
- r_1R , quadrature reactance drop in whole circuit.
- OI_0 , in-phase apparent resistance drop in outer conductor.
- r_0P , quadrature apparent (negative) drop in outer conductor.
- OI_i , total apparent drop in the inner conductor.
- $I_i'I_i$, quadrature drop in inner conductor due to flux in insulator space.
- OI_i' , true apparent drop in inner conductor.

The general nature of the loci of the ends of the apparent inner and outer impedances and the total (actual) equivalent impedance is shown in fig. 5. The reactance due to the

Fig. 5.



Apparent Impedance Vector Loci, showing effect of increasing frequency
(Concentric Cable.)

insulation flux has been omitted, as it increases proportionally with the frequency and rather confuses the point that the diagram is intended to illustrate—namely, the effect of want of uniformity in the current-distribution in the conductors.

CIV. *On Photographing the Ionization Tracks of the Rest Atoms of Radioactive Elements.* By D. M. BOSE, M.A., Ph.D., Ghose Professor of Physics, and S. K. GHOSH, M.Sc., Research Scholar, University College of Science, Calcutta*.

[Plate XIV.]

WHEN an atom of a radioactive substance disintegrates with the emission of an α -particle, the rest atom recoils back in the opposite direction with a velocity $v' = \frac{m}{m'} v$,

where m , v are the mass and velocity of the α -particle, and m' the mass of the rest atom. The value of v' is from 3 to 4×10^7 cm. per sec.

The ionization by these rest atoms has been studied in detail by Wertenstein†. He has shown that though the velocity and kinetic energy of such an atom is about $\frac{1}{55}$ times that of an α -particle, yet the total number of ions produced by such an atom is less than $\frac{1}{100}$ times that produced by an α -particle. On the other hand, he has found that the number of ions produced per cm. length is greater than that produced by an α -particle; in certain cases it was five times greater. Further, contrary to what is observed in the case of α -particles, the number of ions produced per unit length diminishes with the velocity of the rest atom.

The range of the rest atom from RaA was found by Wertenstein to be

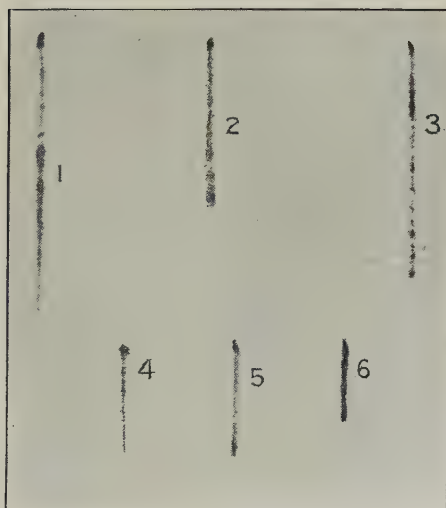
In air at atmospheric pressure	0.14 mm.
In hydrogen	0.83 ,,
In silver about	2×10^{-5} mm.

From the study of the absorption curves he concluded that the scattering of the rest atom is much greater than that of the α -particle, a result which can be expected from theoretical considerations.

It occurred to us that by taking photographs of the ionization tracks of α -particles emitted by the disintegration products of radium emanation contained in a given volume of hydrogen at reduced pressure, it would be possible to get the ionization tracks of the rest atoms too.

* Communicated by the Authors.

† For literature, etc., see Meyer and Schweidler's *Radioaktivität*, pp. 133 & 164. The above account of the ionizing properties of the rest atom has been taken from this book.



The rest atom tracks all point upwards.

From Wertenstein's experiments it was concluded that these tracks would show the following characteristics :—

(i.) They would appear as continuations of the α -particle tracks, but would be thicker at the base and narrower at the end.

(ii.) While the α -particle tracks are straight lines, these would show a considerable amount of scattering.

By means of a modified form of Wilson's apparatus which is described below, we have succeeded in obtaining photographs of the ionization tracks of the rest atoms in hydrogen at a pressure of about 12.5 cm. These tracks show the characteristics which have been mentioned above. It can be stated here at once that, owing to the necessity of having saturated water vapour inside the cloud-chamber the range of the recoiling rest atom inside it, when filled with hydrogen at a given low pressure, is less than what would be expected from Wertenstein's value for the range in hydrogen at atmospheric pressure, viz. 0.85 mm.; *e. g.*, if we take the temperature to be 32° C. (which is about the value that prevailed in the room during this series of experiments), then the tension of saturated water vapour is 3.5 cm., and the range of the rest atom in a vessel filled with hydrogen saturated with water vapour at a pressure of 20 cm. is 1.5 mm. only, while the corresponding value in pure hydrogen under the same pressure is 3.2 mm.

Apparatus.

The essential modification introduced in this apparatus is that while in Wilson's apparatus the expansion is produced by the rapid fall of a piston, here it is produced by opening a valve connecting the cloud-chamber to a vacuum vessel. The apparatus is built on the same principle as the one used by one* of us in photographing the hydrogen recoil atoms. The original apparatus was made entirely of glass, but owing to the difficulty of getting good glass-blowing done here, the present apparatus was made partly of brass. We find that this modification has not in any way diminished the efficiency of the apparatus.

The cloud-chamber C (10 cm. diam. \times 7 cm. depth) is made out of a stoppered-glass bottle, whose bottom is removed and replaced by a glass plate cemented with sealing-wax. To the neck of this bottle is fitted a glass

* D. Bose, *Phys. Zeit.* p. 388 (1916): Berlin Dissertation, 1919.

After the apparatus has been several times washed out with hydrogen, it is filled with hydrogen at the desired pressure as recorded by the manometer M_1 . To produce an expansion all the taps except T_5 are closed and the pump set going. When the pressure indicated by the manometer M_2 is less than that indicated by M_1 , then T_3 is opened. The level of the water falls in B_1 and rises in B_2 . When the level in B_1 has fallen sufficiently low to produce the required degree of expansion, then T_3 is closed and the pump stopped. On lifting the valve the expansion is produced. The apparatus is brought back to its original state by opening T_6 and T_3 . As the water flows back to B_1 the valve V is lifted up, and the tap T_1 opened. The returning gas sweeps in some of the emanation contained in E into the chamber C .

It is found that when the air in B_1 is being pumped out, some of the hydrogen dissolved in the water bubbles out. After the expansion when air is introduced into B_2 , the water dissolves some of the air, and a part of it is given off to the volume enclosed above the water-level in B_1 . Thus after making a certain number of expansions, it is found necessary to replace the hydrogen in the cloud-chamber, otherwise the ionization tracks of the rest atom cease to be visible.

The cylindrical inner surface of C was completely blackened by covering it with a paste of lampblack mixed with Canada balsam dissolved in xylol. A strip of glass surface was left clear for introducing a beam of sunlight, which was focussed into the chamber by means of a lens L and a heliostat. The camera was placed vertically above the chamber C . A Thornton Pickard shutter S was fitted to the objective of the camera. The releasing string of the shutter was tied to the valve-handle H , after passing over a pair of adjustable pulleys. By adjusting the tension of the string, the exposure can be made at a suitable instant to secure the best photographs of the ionization tracks. Sunlight was only introduced into the chamber after the apparatus had been made ready for an exposure.

The objective used was a Dallmeyer lens of aperture $f/3$. There was an arrangement for removing the ions produced in C by means of an electric field, which was cut off when the exposure was made.

Result.

A few photographs are given (Pl. XIV.) in which are shown the simultaneous ionization tracks of the α -particle and the rest atom arising out of a spontaneously disintegrating radioactive atom. That these photographs represent the beginnings and not the ends of α -particle tracks can be seen from the following considerations.

In these experiments the final pressure in C was about 12.5 cm. (with the exception of No. 1 where it was 15 cm.). Under this pressure in hydrogen the ranges of the α -particles from all the disintegration products of radium are several times the linear dimensions of the vessel. Further, we have found that if no emanation is allowed to enter C by closing the tap T_1 , and if the gas in this vessel is removed, then the number of ionization tracks seen at each expansion due to the emission of α -particles from radioactive matter deposited on the inner surface of C is very small; frequently during an expansion not a single track is seen. And these tracks when observed extend from one side of the vessel to the other.

The expansion used in these experiments was about 1.7. The photographs are reproduced on a scale of unit magnification. In all the photographs except No. 4 it will be seen that the ionization tracks are broader at the base and narrower towards the end. All of them show a certain amount of scattering. The rest atom shown in No. 4 we think has been scattered in the direction of the line of sight.

Summary.

A modification of Wilson's expansion apparatus for photographing the tracks of ionizing particles and rays is described.

With this apparatus the ionization tracks of the rest atom of radioactive elements have been photographed.

It was found that these tracks possess the characteristic properties which were deduced by Wertenstein from his study of the ionization produced by rest atoms.

University College of Science,
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Calcutta, India.
Sept. 7, 1921.

CV. *The Elastic Constants of Spruce.* By
H. CARRINGTON, *B.Sc., M.Sc.Tech., A.M.I.Mech.E.**

FROM a consideration of the results of experiments on four balks of spruce†, mean values of the moduli in terms of a unit stress of 10^4 grammes weight per square centimetre are:—

Balk.	E_x .	E_y .	E_z .	F_x .	F_y .	F_z .	μ_{yz} .	μ_{zx} .	μ_{xy} .
A.....	748	421	10,100	24,200	23,000	1,335	621	506	22.65
B.....	864	706	16,900	30,900	45,100	2,170	860	637	35.1
C.....	727	436	10,950	24,500	24,400	1,335	632	506	23.6
D.....	650	424	11,150	23,400	29,100	1,470	602	588	26.1

The axis of z is in the direction of the grain, and the axes of x and y are in directions perpendicular to the grain, and normal and tangential respectively to the annual layers. The direct moduli are noted by E_x , E_y , and E_z ; the symbols F_x , F_y , and F_z are equal respectively to three relations of the type

$$F_x = \frac{E_y}{\sigma_{yz}} = \frac{E_z}{\sigma_{zy}},$$

where $\sigma_{yz} \dots$ denotes $\frac{\text{lateral strain in the direction of } z}{\text{longitudinal strain in the direction of } y}$,

and μ_{yz} , μ_{zx} , and μ_{xy} are the three principal values of the moduli of rigidity.

The moduli correspond with 12 per. cent. of moisture,

* Communicated by the Author.

† Phil. Mag. June 1921, May and July 1922.

and the other physical properties which influence the moduli are:—

Balk.	Density (dry). Grammes/cu.cm.	Shrinkage per cent. in direction.	
		XOX.	YOY.
A	0.371	1.97	3.50
B	0.496	2.86	3.50
C	0.3855	2.15	3.59
D	0.390	1.91	3.84

The elastic constants are the coefficients in the formula for the strain-energy function *

$$2W = Ae_{xx}^2 + Be_{yy}^2 + Ce_{zz}^2 + 2Fe_{yy}e_{zz} + 2Ge_{zz}e_{xx} + 2He_{xx}e_{yy} \\ + Le_{yz}^2 + Me_{zx}^2 + Ne_{xy}^2,$$

this being written in the notation of Love's 'Elasticity.' These coefficients can be calculated from the values of the moduli. Values of A, B, and C are given by three equations of the type

$$A = \frac{1}{E_y E_z} - \frac{1}{F_x^2},$$

and values of F, G, and H by three equations of the type

$$F = \frac{1}{E_x F_x} + \frac{1}{F_y F_z},$$

$$\text{where } \Delta = \begin{vmatrix} \frac{1}{E_x} - \frac{1}{F_z} - \frac{1}{F_y} \\ -\frac{1}{F_z} & \frac{1}{E_y} - \frac{1}{F_x} \\ -\frac{1}{F_y} - \frac{1}{F_x} & \frac{1}{E_z} \end{vmatrix},$$

whilst L, M, and N are equal respectively to μ_{yz} , μ_{zx} , and μ_{xy} .

* Love's 'Elasticity,' Art. 110.

On inserting the values of the moduli given in the first table in these equations, the following table of elastic constants results. The constants are in terms of a unit stress of 10^4 grammes weight per sq. cm.

Balk.	A.	B.	C.	F.	G.	H.	L.	M.	N.
A.....	984	550	11,000	369	564	388	621	506	22.65
B.....	1,100	863	18,150	606	589	437	860	637	38.1
C.....	1,015	607	12,650	424	608	495	632	506	23.6
D.....	1,005	500	11,000	385	579	396	602	588	26.1

It immediately becomes evident from an examination of these results that Cauchy's deduction *, i. e. $F = L$, $G = M$, and $H = N$, does not hold, for H is over ten times as great as N . It therefore follows that the equations of St. Venant †, which were based on the assumption of the truth of this reduction, do not apply. If these equations had held, they would have reduced the number of constants from nine to four. The equations were reduced in default of experimental results for which St. Venant observes the need.

If the spruce can be considered as transversely isotropic, then $A = B$, $F = G$, $L = M$, and $A - 2N = H$, so that the number of constants is reduced from nine to five. It is easily seen that these relations do not apply, and in particular that $A - 2N$ is in every case over twice as great as H . In view of the large number of experiments from which the constants are calculated, the last difference is too great and consistent to be accounted for by variations in the æolotropy of the material.

It accordingly appears that neither Cauchy's reduction nor transverse isotropy hold for spruce. It may be noted that Voigt ‡ found from experiments on the elasticity of crystals that, on the whole, Cauchy's reduction did not apply.

* *Ibid.* Art. 66.

† Todhunter & Pearson's *Elasticity*, vol. ii. Arts 307-314.

‡ Love's *Elasticity*, Art. 113 and Introduction.

CVI. *The Physics of Colour Vision.**By Prof. W. PEDDIE*.*

THE subject of colour vision is one which appeals almost equally to the physicist, the physiologist, and the psychologist. But it is rarely indeed that a writer on the subject is equally qualified to deal with the several aspects. As a matter of fact, it is probable that, with the exception of Helmholtz himself, no one was ever in that position. The experimental physicist deals with the observational facts, and the mathematical physicist deals with their formal relationships. He may, at the same time, introduce a hypothetical mechanism for the elucidation of the reasoning. That mechanism may, or it may not, be ultimately found to be the one actually occurring. The settlement of that question is one for the anatomist or the physiologist. But their settlement of it, when it comes, must be in agreement with the fundamentally essential mathematical formulation as determined by the physicist. And that formulation, developed initially by Helmholtz, is now so complete that the trichromatic theory of vision must be regarded as being established physically, in its main features, on as firm a basis as is the molecular theory, or the electromagnetic theory of light.

Much needless discussion and inconsequent assertions would be prevented were any physiologist, who may happen not to have had the leisure or the training essential to a full comprehension of the bearing of the physical theory, to work out his problems and conclusions in his own way, using his own terminology, and leave its correlation with physical theory to the physicist. There is, for example, no reason really why Dr. Edridge-Green, with his wide observational experience, should not express his results in terms of a score of fundamentals if he so thinks proper. We may leave their subsequent reduction to three, if found possible, to the physicist. The collaboration between the physiologist and the physicist should be complete. Instead of that there is far too often found repeated attacks by physiologists upon certain aspects of physical theory, which are supposed by them to be irreconcilable with facts; the conclusion being due, in many cases, to an insufficient, and probably unavoidably so, familiarity with the physical reasoning.

It is with the hope that this state of matters may become less evident, and that the co-operation of physiologists and

* Communicated by the Author.

physicists may speedily become more complete and fruitful, that I venture to discuss some observational facts, in view of the recent attack by Dr. Edridge-Green upon the trichromatic theory in the November number of this Magazine.

He quotes from Helmholtz the statement that, as far as he could see, there was no means of deciding on the elementary colour sensations other than the examination of the colour-blind. But Dr. Edridge-Green seemingly does not know that this statement has reference necessarily to the early view that colour-blindness was due only to absence of one of the three fundamentals. When Helmholtz found that there were cases of colour-blindness which did not fall into that category, he gave the natural extension of the theory of dichromasy, quite sufficient to cover all observed cases of the abnormality, and more. The result was that he pointed out clearly that it is utterly impossible to discriminate the absolute fundamentals by means of observations on colour mixture. Dr. Edridge-Green surely has not observed that Helmholtz's conclusion is dependent only on the linearity of the law of colour mixture, and is, therefore, quite independent of any assumption as to trichromasy. Thus it applies equally to his own multi-chromatic or non-elemental postulates. Helmholtz's position is exactly counter to Dr. Edridge-Green's aim, instead of supporting it as he claims. His crucial facts are absolutely non-crucial.

In discussing the relation of luminosity to colour he then states, that if the sensation of white were compounded by the addition of three elementary processes, and one of these processes were subtracted, the position of the apex of the luminosity curve would not be the same in the colour-blind as in the normal. Here he must mean that it is to be assumed that the apex of the subtracted curve does not coincide with the luminosity apex. But in any case, it is pointless to refer only to the limited, simplest, and therefore first adopted postulate, as to the mode of occurrence of dichromasy. From this point of view his next statement, that there are numerous dichromics who have a luminosity curve similar to the normal, ceases to have application as an adverse argument. The implied inference is that the trichromatic theory cannot meet the case. On the contrary, this dichromatic type is one of the most easy to predict on the basis of that theory. Then he refers to a case of dichromasy in which there was shortening of the red end of the spectrum while the luminosity apex was in the normal position. This is readily accountable for on the trichromatic theory; but the equation which Dr. Edridge-Green writes down as a trichromatic expression for the

theoretical white is not one which any physicist upholding that theory would write down as the suitable expression.

He then asserts that the facts of colour-blindness are quite inconsistent with any three-sensation theory, and that supporters of such an elemental theory have in many cases contented themselves with describing a case of colour-blindness in the terms of the theory, without showing that the ascertained facts are consistent with the theory. This fairly well amounts to a charge of incompetence, or at the very least, of peculiar oversight. No upholder of the trichromatic theory can claim infallibility; but it is logically impossible to describe in terms of a physical theory, facts which are inconsistent with it. The alternative explanation, which is rendered likely by some of his other statements regarding the theory, is that Dr. Edridge-Green is himself unacquainted with the full scope of the theory. Thus he states, as an example, that no one has shown how, on an elemental theory, 50 per cent. of dangerously colour-blind can get through the now obsolete wool test. If there be any truth in this statement, and it may easily be entirely true, it can only mean that practically everyone is aware of the ease with which the explanation is furnished by the trichromatic theory; in fact, the explanation is identical with that given by Dr. Edridge-Green himself. That it must be so is self-evident to anyone who realizes the essential linearity of the law of colour mixture. Then he asks, as if unanswerable on the trichromatic view, two questions whose solution should be easily given by anyone who realizes the most general way of imposing six relations amongst nine arbitrary quantities.

The next case discussed is one of merely anomalous vision, in which little more than one-half of the normal amount of green was used in forming an equation for white, and fatigue by red diminished the necessary proportion still further. I have known a case of this type in which a colour which was reddish to a normal eye appeared to be greenish to the abnormal eye. The trichromatic explanation is very direct, and Dr. Edridge-Green does not, in this case, make any direct assertion that the effect is not so explainable.

His remarks upon the inadequacy of the terms red-blind and green-blind, as frequently used, may be readily agreed with, although they are only in the same category as other terms, such as latent-heat, which are survivals of an earlier provisional hypothesis, and do no harm when their limitations are comprehended.

He points out the interesting fact that some colour-blind

persons, who object to a normal white equation, cease to do so when the intensity of the comparison white is raised to such an extent that it appears much too bright to the normal eye. He remarks that this clearly shows that the normal mixed white produces the same effect so far as colour is concerned, but has a more powerful effect as to luminosity. This may be so; but it need not indicate anything more than the change of sensation with intensity. However that may be, when he goes on to say that these facts are quite inconsistent with a hypothetical red sensation, which is affected by light of all visible wave-lengths, it is not possible to agree. He points out that the red end of the spectrum is always shortened in these cases, and, in illustration of his argument, proceeds thus: "A man with shortening of the red end of the spectrum and normal colour discrimination will put together as exactly alike a pink and a blue or violet much darker. If, however, the pink and blue be viewed by a normal-sighted person through a blue-green glass which cuts off the red end of the spectrum, both will appear identical in hue and colour. This proves conclusively that the defect is not due to a diminution of a hypothetical red sensation, because all the rays coming through the blue-green glass are supposed to affect the red sensation, and yet we have been able to correct the erroneous match by the subtraction of red light." Surely it is the case that abstraction of red light from the pink by the blue-green transmitting glass gives rise to less red stimulus, so that the pink looks blue. There is in his statement a fundamental misconception of the implications of the trichromatic theory, which is not by any means uncommon.

The remark is next made that "A totally erroneous view of a case may be obtained through methods based on the three-sensation theory." And, in illustration of this, he discusses a particular case of colour-blindness, and gives an explanation of it, which he apparently presumes to be impossible on the trichromatic theory. Yet the argument could practically be adopted word for word by one accounting for the phenomena on a trichromatic basis.

Finally, Dr. Edridge-Green appeals to Dr. Houstoun's theory as supporting his own special views. It seems to me, on the contrary, that the theory is worthy of consideration as giving a possible indication of the way in which trichromasy has arisen.

He does not seem to be aware of the fact that Helmholtz insisted on the merely illustrative value of the special hypothesis regarding the mechanism of vision, and even said that

a triple set of nerve-fibres might be inessential. The fact that Helmholtz nevertheless did not give up trichomasy might give food for thought. On the other hand, the fact that physiologists very frequently take wrong views of the contents of the trichromatic theory can scarcely be altogether laid to their blame. Knowledge of the earlier developments was spread abroad, and was incorporated in text-books and discussions, and was never superseded fully by the later treatment. Most of the arguments directed against it are futile, in that they are aimed at the older views, and, even so, frequently regard inessentialities as essential. The magnificent structure finally reared by Helmholtz is to this day largely unknown, although it is adequate for the treatment of the most modern work of observation.

CVII. *Quantum Theory of Photographic Exposure.*
*Third Paper. By L. SILBERSTEIN, Ph.D.**

[Communication No. 173, from the Research Laboratory of the Eastman Kodak Company.]

THE purpose of this paper is, first, to take account of the absolute energy values of the exposures used in the experiments described in the first two papers on this subject, which values were since measured, and, in the second place, to deduce from the fundamental formula the integral or "density" formula for a certain type of emulsions and to compare it with the experimental results recently obtained with X-rays. The treatment of the first point will afford a good opportunity for amplifying the proposed theory in a sense already hinted at in the second paper.

1. In section 4 of the second paper (Phil. Mag. vol. xliv. 1922, p. 956), it was mentioned that possibly not the whole but only some fraction ϵ of the area a of a silver halide grain is "vulnerable," i. e. ready to become developable (say, to lose an electron) on being hit by a light dart carrying a quantum of energy of sufficiently high frequency, and that if n be the unknown number of such darts impinging per unit area of the plate, what can be determined from microphotographic experiments alone is essentially only the product nea , and therefore also $n\epsilon$, but not n itself. Whether at all and how much the coefficient ϵ , which can be taken as the measure of sensitivity of a given material, differs from unity,

* Communicated by the Author. Paper read at the annual meeting of the American Physical Society at Boston, December 27th, 1922.

can only be decided by measuring the absolute energy-value of the exposure given to the plate. If this be E per cm.² of the plate, we shall have (assuming that the whole energy is split into quantum parcels)

$$E/h\nu = n,$$

and dividing by this number the value of ϵn obtained microphotographically, we shall find the required value of ϵ .

Now, Trivelli and Richter's "first step" observations which were tabulated in the first paper and for which the microphotographic method gave $\epsilon n = 0.572$ per square micron, *i. e.*

$$\epsilon n = 5.72 \cdot 10^7 \text{ per cm.}^2,$$

was obtained by an exposure to a 250 watt nitrogen lamp at a distance of one metre, through a standardized diaphragm (No. 10) with a standardized opal glass and through a blue filter (referred to as No. 78, giving a maximum intensity at $\lambda = 470\mu\mu$) during 45 seconds. Careful measurements recently completed in this laboratory by Mr. A. L. Schoen have shown that that exposure amounted, within ± 10 per cent., to

$$E = 19.8 \text{ ergs/cm.}^2,$$

i. e., with $\lambda = 470\mu\mu$, to $n = 4.7 \cdot 10^{12}$ light quanta per cm.² of the photographic plate. This also is, substantially, the number of quanta reaching the plane of the (single) layer of grains, for the reflexion at the surface of and the absorption within the thin gelatine layer amount but to a few per cent.

In our case, therefore, *i. e.* for the experimental emulsion W12C used in those observations, the discussed fraction would be as small as

$$\epsilon = 1.2 \cdot 10^{-5}.$$

In fine, on an average, only about one hundred thousandth, and certainly *not more than one ten thousandth*, of the area of a grain of this emulsion would be sensitive to light, *i. e.*, made developable (together with the remainder of the grain) on being hit by a single light dart*. There being good

* Mathematically, the above state of things might be accounted for by assuming that the whole area of a grain is sensitive, but that a "light dart" carries 10^4 or 10^5 quanta of energy. From the physical standpoint, however, such an assumption, made *ad hoc* and standing perfectly isolated, is manifestly very unsatisfactory as compared with that attributing to each light dart a *single energy quantum*. For there is good independent evidence for the existence and separate propagation of precisely such energy parcels.

At first sight yet another alternative might seem possible, namely, to assume that the whole area of a grain is equally "sensitive," but that

reasons for ruling out the alternatives mentioned in the footnote, we are driven to this conclusion by the above experimental results. This does not necessarily mean that only such a small fraction of the impingent light darts is actually absorbed by the grain (the remainder being transmitted and reflected), but that only such a small minority of all these darts are photographically efficient, *i. e.*, do actually eject photoelectrons.

It may be well to point out in this connexion that in a set of Elster and Geitel's experiments (1912) with what was considered a very sensitive potassium cell, only one out of 2300 blue light quanta hitting the cell liberated a photoelectron, though a little later (1913) Pohl and Pringsheim succeeded in pushing the efficiency of a potassium surface under special conditions up to two or even three in a hundred. (*Cf.* A. L. Hughes, Photo-Electricity, 1914.)

Moreover, the replacing of the measured grain area a by ϵa introduces into the proposed theory, at first purely geometrical, a very desirable feature, namely the coefficient ϵ which may vary from emulsion to emulsion, and will thus serve as a measure of their specific sensitivity. The fact that this coefficient was found to be as small as 10^{-4} or 10^{-5} is also of some practical interest; for it makes it reasonable and worth one's while to try to increase it considerably, pushing it towards its ideal limit, which would be unity.

We have thus far tacitly assumed that, for equal grains at least, ϵ is a given constant fraction, and this amounted simply

instead of one, it must be hit by at least, say, a thousand light quanta in order to be made developable. But such an assumption would entirely distort the original formula

$$k/N = 1 - e^{-s}, \quad s = \text{const. } E a,$$

which essentially, apart from minor correction terms, does represent the microphotographic findings. In fact, while the number of grains hit at least *once* is

$$k = N(1 - e^{-na}),$$

the number of those hit at least *twice* will be found to be

$$k_2 = k \left(1 - e^{-\frac{m-k}{k}} \right), \quad m = nNa,$$

and the number of those hit *three times*

$$k_3 = k_2 \left[1 - e^{-\frac{m-k_1-k_2}{k_2}} \right],$$

and so on, and these formulæ deviate considerably, and to an increasing extent, from the correct one.

to replacing na in our previous formulæ by nea . The main results will not be altered very much if this simple assumption is replaced by the following more general one which is more likely to correspond to the actual conditions, and seems fruitful inasmuch as it leads to some further interesting experiments.

Let the sensitive part of the area of a grain, instead of being all in a lump, consist of a number of separate vulnerable or *sensitive spots*, each of area ω , and distributed among the individual grains (each of area a) not equally but *haphazardly*. The necessary and sufficient condition for a grain to be made developable will now be that at least one of its spots should be hit by at least one light dart of a sufficiently short wavelength*.

Let N be the total number of grains, of equal areas a , and N_0, N_1, N_2 , etc., the numbers of those among them which have 0, 1, 2, etc., generally κ such vulnerable spots. Then the number of grains affected by an exposure to n light darts will be, by our original formula (without the correction due to a finite "cross-section of the darts," which now may become superfluous),

$$k = \sum_{\kappa=0}^m N_{\kappa} (1 - e^{-\kappa n \omega}),$$

if m be the largest number of spots on a grain. Since

$$N = \sum N_{\kappa},$$

this can be written

$$k = N - \sum_{\kappa=0}^m N_{\kappa} e^{-\kappa n \omega}.$$

Now, if $\bar{\kappa}$ be the average number of spots per grain, the former being distributed haphazardly among the latter, we shall have

$$\frac{N_{\kappa}}{N} = \binom{N_{\bar{\kappa}}}{\kappa} \frac{1}{N^{\bar{\kappa}}} \left(1 - \frac{1}{N}\right)^{N\bar{\kappa} - \kappa},$$

* These vulnerable "spots" will not be confounded with Prof. Svedberg's "centres" (mentioned in our second paper), which he himself considers as the product of light action on the halide grains. The "spots" would rather correspond to the nuclei of sensitiveness suggested by Mr. F. F. Renwick (Brit. Journ. of Photogr. lxviii. 1921, p. 607). It seems likely that Svedberg's "centres" are those of our sensitive spots which were actually hit and thus made developable. If so, then a sufficiently strong exposure should reveal (after a short development) all "spots" as visible markings or "centres."

and for large $N\bar{\kappa}$ and small $\kappa/N\bar{\kappa}$,

$$N_{\kappa} = N \frac{\bar{\kappa}^{\kappa} e^{-\bar{\kappa}}}{\kappa!}, \quad \dots \quad (A)$$

and therefore,

$$\frac{k}{N} = 1 - e^{-\bar{\kappa}} \sum_0^m \frac{\bar{\kappa}^{\kappa} e^{-\bar{\kappa}}}{\kappa!}.$$

Here we can write

$$\Sigma = \Sigma \frac{(\bar{\kappa} e^{-n\omega})^{\kappa}}{\kappa!},$$

and if m be a large number (a condition still compatible with a small ratio $m : N\bar{\kappa}$),

$$\Sigma = e^{\bar{\kappa} e^{-n\omega}}.$$

Thus our formula becomes

$$k = N[1 - e^{\bar{\kappa}(e^{-n\omega} - 1)}]. \quad \dots \quad (1)$$

If $n\omega$ (a pure number) is a small fraction, we have

$$e^{-n\omega} - 1 \doteq -n\omega,$$

and, as a first approximation,

$$k = N[1 - e^{-n\bar{\kappa}\omega}],$$

as if every grain had actually the average number $\bar{\kappa}$ of spots and, therefore, the same vulnerable area $\kappa\omega$. The second approximation, up to $(n\omega)^3$, will be

$$k = N[1 - e^{-n\bar{\kappa}\omega(1 - \frac{1}{2}n\omega)}]. \quad \dots \quad (1a)$$

Introducing again the abbreviation

$$v = \log \left(\frac{N}{N - k} \right), \quad \dots \quad (2)$$

the first and the second approximations can more conveniently be written $v = \bar{\kappa}n\omega$ and

$$v = \bar{\kappa}n\omega(1 - \frac{1}{2}n\omega) \quad \dots \quad (3a)$$

respectively, and the complete formula (1),

$$v = \kappa(1 - e^{-n\omega}). \quad \dots \quad (3)$$

The product $\kappa\omega$ is the average vulnerable area of a grain, and since a is its total (projected) area, our coefficient ϵ , called provisionally "the specific sensitivity," will now be defined by

$$\epsilon = \frac{\bar{\kappa}\omega}{a} = \left(\frac{\kappa\omega}{a} \right), \quad \dots \quad (4)$$

and will thus represent the *average sensitivity* of the (equal) grains of the emulsion. We do not prejudice whether ϵ itself is a constant of the material or depends on a . In other words, κ may but need not be proportional to the area of the grain. Using the definition (4), the approximate formula (3a) can be written

$$v = \epsilon a n (1 - \frac{1}{2} \epsilon a n / \bar{\kappa}). \quad (5a)$$

As far as our present knowledge goes, the second bracketed term need not be a negligible fraction of unity. This will depend on κ . In fact, the value of v observed in all our experiments, even for such grains as $a = 2\mu^2$, was of the order of 0.5. Thus, since $v \doteq \epsilon a n$ gives at least a coarse approximation, the product $\epsilon a n$ itself is, in all these cases, a moderate fraction. Consequently the second term $\epsilon a n / 2\bar{\kappa}$ need not be inappreciably small unless $\bar{\kappa}$, the average number of vulnerable spots per grain, is large.

We will, for the present, close the discussion of the complete equation (3), equivalent to (1), by one more remark. If this equation be accepted as valid even for indefinitely increasing exposure, $\bar{\kappa}$ acquires a simple experimental meaning and is made easily accessible to measurement, namely, it becomes equal to the limiting value of v for $n = \infty$,

$$\bar{\kappa} = v_{\infty} \equiv \log \frac{N}{N - k_{\infty}}, \quad (6)$$

or, equivalently, $k_{\infty} = N(1 - e^{-\bar{\kappa}})$ *. Thus, if κ is reasonably small, the limiting number k_{∞} of affected grains (of a given size) should perceptibly fall short of the total number N of grains originally present; the surviving grains would simply be those that had no vulnerable spots at all. Whether, and to what extent, such be the case can only be decided by careful experiments with a rather fine-grained emulsion. Notice that if $\bar{\kappa}$ amounts to more than a few units, the percentage value of k_{∞} will not be easy to distinguish microphotographically from 100. The utmost which can thus be reliably distinguished can be taken to be 99 per cent., *i. e.* 1 per cent. surviving grains, to which would correspond $\bar{\kappa} = 4.606$: in order to obtain 10 per cent. of permanently surviving grains, the value of $\bar{\kappa}$ would have to be about

* Notice that this is only a verification of (3) with regard to the original assumption, according to which all grains deprived of vulnerable spots (N_0 in number) should be left over. In fact, we have by (A), $N_0 = N e^{-\bar{\kappa}}$, and since, by the said assumption, $k_{\infty} = N - N_0$, formula (6) follows at once.

2.30 only. For small grains, however, $\bar{\kappa}$ may be small enough to enable us to distinguish decidedly k_{∞} from N .

If so, then, having found $\bar{\kappa}$ by means of (6), we shall be able to determine ω by means of (3) which, n being measured, will give

$$\omega = \frac{1}{n} \log \frac{v_{\infty}}{v_{\infty} - v}. \quad \dots \dots \dots (7)$$

In this way we may be able to find both κ and ω experimentally, for every grain size a , instead of speculating about their dependence upon a .

The results of experiments just undertaken to that effect by my colleague Mr. Trivelli will be related in the next paper.

2. Density formula for ideally "exponential" emulsions*.—

It has seemed interesting to test the elementary formula $k = N(1 - e^{-\epsilon n a})$ with ϵ assumed constant, by integrating it for an emulsion of exponential type and comparing the resulting formula with the usual density measurements on a plate coated with an emulsion of roughly such a type.

If the number of grains of size a to $a + da$ is $N_a da = f(a) da$, with

$$f(a) = C e^{-\mu a}, \quad \dots \dots \dots (8)$$

valid from $a = a_1$ to $a = a_2$ (and nil outside these limits), then the total projected area of AgBr made developable will be

$$K = A - \frac{A \mu^2}{(\epsilon n + \mu)^2} \left| [1 + (\epsilon n + \mu) a] e^{-(\mu + \epsilon n) a} \right|_{a_2}^{a_1},$$

where $A = \int a f(a) da$ is the total available area of the silver halide.

If the frequency curve has a long "tail," as is the case with many emulsions, we can approximate the real case by taking $a_2 = \infty$, and, on the other hand, if a_1 is small enough, we can simplify matters, without much deviating from the actual conditions, by putting $a_1 = 0$. Thus the last formula becomes

$$K = A - \frac{A \mu^2}{(\epsilon n + \mu)^2} \dots \dots \dots (9)$$

The photographic "density" is always assumed to be

* *I. e.*, emulsions whose frequency-curves assume an exponential form, as defined by (8); this is, approximately, the case for many emulsions.

proportional to the blackened mass of silver halide*. If so, then denoting by D_m the "maximum density," or rather the extreme density obtainable,

$$D = D_m \left[1 - \frac{\mu^2}{(\epsilon n + \mu)^2} \right]. \quad (10)$$

Notice that D depends only on the quotient $\epsilon n/\mu$.

On the other hand, if the transparency T of the plate is taken to be

$$T = 1 - K,$$

the corresponding density will be (writing Log for \log_{10})

$$D = -\text{Log}(1 - K), \quad (11)$$

of which the former relation is an approximation (for small K). At any rate, it has seemed interesting to combine also this relation (11) with the formula (9) for the blackened area K . This, with the abbreviation

$$\frac{\epsilon n}{\mu} = \alpha E, \quad (12)$$

gives for the density D as function of the exposure E , in any conventional units,

$$D = -\text{Log} \left[1 - K_m + \frac{K_m}{(1 + \alpha E)^2} \right], \quad (13)$$

where K_m is defined by

$$D_m = -\text{Log}(1 - K_m). \quad (13a)$$

Now, in most practical cases (of many-layered coatings, of course) the extreme density D_m certainly exceeds the value 3, so that $1 - K_m < 0.001$. For plates producing such high densities we may use the limit of (13) for $K_m = 1$ (i. e. for $D_m = \infty$), which gives

$$D = 2 \text{Log}(1 + \alpha E). \quad (14)$$

* This is based on experimental results obtained with *many-layered* coatings for densities ranging from 0.5 to 3.5 (cf. Sheppard and Mees. Investigations on the Theory of the Photographic Process, p. 38). The matter has been investigated mathematically by P. G. Nutting (Phil. Mag. xxvi. p. 423 (1913)). For a one layer coating the proportionality between density and mass of silver does not hold, the correct relation being, manifestly, T (transparency) $= 1 - K$, whence

$$D = \text{Log} \left(\frac{1}{T} \right) = -\text{Log}(1 - K),$$

so that only for small K , $D = MK$, where Log stands for \log_{10} , and $M = \text{Log } e$.

It has seemed interesting (even apart from any theory) to compare this remarkably simple formula with some experimental "characteristic curves," especially with X-ray exposure curves which appeared to be qualitatively at least of such a type. Although the relation (11), upon which (14) is based, is suited primarily to single-layer plates, yet the latter formula might be expected to hold also, approximately at least, for many-layered coatings, provided the emulsion has, roughly, an exponential effective frequency curve. The following table contains the results of such a comparison. The first column gives the X-ray exposures E in arbitrary units (in this case, proportional to the exposure times, at reliably constant intensity), and the second column the corresponding densities obtained in this laboratory by Mr. R. B. Wilsey on a "portrait film," the development conditions and time being the same for the whole set of fourteen exposures.

E .	$D_{\text{obs.}}$	$D_{\text{calc.}}$	δD .
1	0.08	0.12	+0.04
$\sqrt{2}$	0.15	0.17	+0.02
2	0.20	0.23	+0.03
$2\sqrt{2}$	0.29	0.30	+0.01
4	0.40	0.41	+0.01
$4\sqrt{2}$	0.54	0.54	0.00
8	0.72	0.69	-0.03
$8\sqrt{2}$	0.90	0.87	-0.03
16	1.10	1.07	-0.03
$16\sqrt{2}$	1.32	1.29	-0.03
32	1.56	1.53	-0.03
$32\sqrt{2}$	1.80	1.79	-0.01
64	2.12	2.06	-0.06
$64\sqrt{2}$	2.48	2.33	-0.15

The third column contains the density values calculated by means of (14). The constant being given the value

$$\alpha = 0.151,$$

all the observations, in the wide range of $E = 1$ to 64, and even to $64\sqrt{2}$, are well represented. The deviations δD are all, with a possible exception of the last, well within the limits of experimental error.

Rochester, N.Y.,
January 23, 1923.

CVIII. *Ionization by Collision in Helium.* By J. S. TOWNSEND, M.A., F.R.S., Wykeham Professor of Physics, Oxford*.

1. **T**HE ionization of argon and helium by the collisions of electrons and positive ions with molecules of the gas was investigated some years ago by Gill and Pidduck †, and the experiments which they made on the currents between parallel plates indicated that these processes of ionization follow the same general laws in the monatomic gases as had previously been found with other gases.

These experiments are not in agreement with the modern views held by some physicists as to the mode of development of currents in monatomic gases, or with the determinations of resonance potentials or ionization potentials as found by experiments where the electrons from a hot filament pass through a gauze between two fields in which the electric forces act in opposite directions.

The apparatus used in the latter experiments resembles the three-electrode valve used in wireless telegraphy; and this method of investigation may be referred to as the valve method in order to distinguish the results from those obtained by measuring the conductivity between parallel plates.

When electrons are emitted from the negative electrode in a gas, and the stream flows to a positive electrode at various potentials, the curve representing the currents in terms of the potentials should, according to the modern theory, be in the form of a series of well-defined steps with angular points at the top and bottom of each step; and when experimental results conflict with this view, the discrepancies are attributed to impurities.

2. I have recently made some experiments with Mr. Ayres on the currents through helium, in order to examine the matter more closely by finding a large number of points on the current-potential curve, as in Gill and Pidduck's earlier experiments these points are far apart, and variations in curvature might have escaped observation. We have taken every precaution to eliminate impurities, and have obtained exactly the same results with helium from a natural source, and helium prepared by heating thorianite. The current-potential curves do not show any steps over the range of forces and pressures similar to those used in Gill and

* Communicated by the Author.

† E. W. B. Gill and F. B. Pidduck, *Phil. Mag.* (6) xvi. p. 280 (1908), and xxiii. p. 837 (1912).

Pidduck's experiments, where the current increased with the potential V , which was proportional to the distance x between the plates, by the factor ϵ^{ax} .

The earlier investigations having been made with a view to testing the theory of ionization by collision and applying it to calculate the sparking potentials, the smallest potentials used in the experiments were generally not less than about 40 or 50 volts. This was necessary in order that the electrons set free from the negative electrode should travel a short distance through the gas and attain the steady motion corresponding to the ratio of the electric force X to the pressure of the gas p .

In the experiments which we have recently made the investigations have been extended, in order to determine the initial effects obtained with comparatively small potentials, where the electrons set free from the negative electrode are being accelerated and begin to acquire sufficient energy to ionize molecules by collisions.

I have recently pointed out in a paper published in the *Philosophical Magazine* * some objections to the principles on which the modern theory of the mode of development of currents is founded, assuming the conclusions which have been drawn from the valve experiments to be correct.

In the case of helium the rate of increase of the currents between parallel plates, with the potential difference between the plates, is much greater than the increase which would be obtained if the energy required to ionize a molecule were as great as 21 or 25 volts, which are the minimum ionizing potentials determined by different investigators using the valve method.

It is of importance, therefore, to show how the energy required to ionize a molecule may be investigated by experiments on currents between parallel plates without introducing any hypotheses depending on the lengths of mean free paths of electrons, or on the mode of distribution of energy about the mean value in a group of electrons.

3. When the conductivity between parallel plates is obtained by the action of ultra-violet light on the negative electrode, and the potential difference \bar{V} between the plates is proportional to their distance apart x , the rate of increase of the current with the potential varies for different ranges of the distance.

In general three ranges may be considered. In the first range, where V is small and the distance x varies from 0 to a , the mean kinetic energy of the electrons and the distribution

* *Phil. Mag.* March 1923.

of the energy about the mean value changes with the distance; in the second range between the distances $x=a$ and $x=b$ the mean kinetic energy of the electrons and the distribution of the energy is independent of the distance x , and the current between the plates is given by the formula $n=n_0e^{ax}$; in the third range from $x=b$ to $x=S$ the positive ions produce an appreciable effect, and sparking takes place at the distance S between the plates. The distances a and b are not very definite and there is no abrupt change in the mode of development of the current. For the purposes of this investigation it is necessary only to consider the rate of increase of the current with the distance between the plates in the first two ranges.

The unit of energy may be taken as the energy acquired by an electron in moving between points differing in potential by a volt, and the energies may be expressed in volts. If c be the energy required to ionize a molecule, ionization may occur when an electron with kinetic energy greater than c collides with the molecule. The probability of a molecule being ionized by a collision depends on the amount by which the energy of the electron exceeds c .

Let $c+r$ be the mean energy of the electrons in coming into collisions which result in the ionization of molecules. After a collision the excess of energy v may be retained by the colliding electron, or some fraction of it may be imparted to the electron which is set free from the molecule. Hence after the collision the mean energy of these two electrons is $\bar{v}/2$. As these electrons starting with the mean energy $\bar{v}/2$ move through the gas under the action of the electric force, their velocities gradually increase until they again acquire sufficient energy to ionize molecules. The electrons pass through this cycle several times, and in addition to the loss of energy when molecules are ionized, they lose energy in each cycle by collisions with other molecules. Let w be the average value of the total energy lost by each electron in a cycle by collisions with molecules which are not ionized.

4. Let \bar{u} be the mean energy of the electrons passing any plane between the two planes $x=a$ and $x=b$, where the motion is steady and the distribution of the energies of the electrons about the mean value \bar{u} is the same at all points between these planes. The number of electrons n that pass through any plane at a distance x from the negative electrode is given by the formula $n=n_0e^{ax}$, which has been found experimentally.

The energy acquired by the stream of electrons as they

pass through the distance $b-a$ is

$$X \int_a^b n_0 \epsilon^{ax} dx = \frac{X(n_2 - n_1)}{\alpha},$$

X being the electric force in volts per centimetre, n_1 the number of electrons entering the space through the plane $x=a$, n_2 the number passing out through the plane $x=b$. The energy of the electrons entering the space is $n_1 \bar{u}$, the energy of those passing out is $n_2 u$, and the energy lost in generating $(n_2 - n_1)$ electrons by collisions is $(n_2 - n_1)c$. Hence

$$\frac{X(n_2 - n_1)}{\alpha} = (c + \bar{u})(n_2 - n_1) + W, \quad \dots \quad (1)$$

where W represents the loss of energy in collisions with molecules which are not ionized. In order to find W in terms of the mean energy \bar{w} lost in a cycle, the distance $(b-a)$ may be taken as the distance in which the current is doubled, so that $n_2 = 2n_1$. In this case each electron entering the space performs one complete cycle, and the total energy it loses in collisions with molecules which are not ionized is \bar{w} .

The electrons generated in the space between the planes perform the first part of the cycle, in which their energy increases from the initial mean value $\bar{v}/2$ to the mean value \bar{u} , in moving various distances under the electric force. Thus the new electrons lose less than the original electrons, and their average loss may be represented by $\bar{w}y$, where y is a factor less than $\cdot 5$.

Hence $W = n_1 \bar{w}(1 + y)$, and equation (1) becomes

$$\frac{X}{\alpha} = c + \bar{u} + \bar{w}(1 + y). \quad \dots \quad (2)$$

5. A relation between c and \bar{v} may be obtained by considering the effect of the two groups of electrons passing the plane $x=a$ with the average energies $\bar{v}/2$ and $c + \bar{v}$ respectively, when $n_2 = 2n_1$. The factor $\epsilon^{(b-a)a}$ is then equal to 2, so that $(b-a) = \cdot 693/\alpha$. Thus each electron entering the space between the two planes ionizes one molecule, except some of those with energies less than the mean value $\bar{v}/2$, the deficiency being made up by some of those with energies greater than the mean value $c + \bar{v}$, which ionize two molecules. The effect as far as the estimate of the mean value of \bar{v} is concerned is the same as if each electron in the two groups ionized one molecule in the space between the two planes. The group passing the plane $x=a$ with the mean energy $\bar{v}/2$

acquires additional energy as it moves under the electric force and ionizes molecules just before passing through the plane $x=b$. The mean loss of energy of each electron in this group due to collisions with molecules which are not ionized is \bar{w} , and the energy each acquires under the electric force is $X(b-a)$. Also for each electron entering the space with the energy $\bar{v}/2$ two pass out with the same mean energy, so that the following relation is obtained

$$\frac{X}{\alpha} \times .693 = c + \bar{w} + \bar{v}/2. \quad . \quad . \quad . \quad (3)$$

6. The values of α corresponding to various forces and pressures may be found experimentally, and the ratio α/p may be represented in terms of X/p by means of a curve.

There is a maximum value of the ratio α/X at the point of contact of the tangent through the origin. In helium the value of α/p is .5 and of X/p is 16 at this point, and the corresponding value of $\frac{X}{\alpha} \times .693$ is 22.2 volts. It is therefore

seen from equation (3) that the sum of the three energies ($c + \bar{w} + \bar{v}/2$) has a minimum value which is 22.2 volts, when $X/p = 16$. The energy \bar{w} diminishes and \bar{v} increases as X/p increases, and assuming c to be constant, the variation in the quantity $\bar{w} + \bar{v}/2$ with the ratio X/p is obtained from the curve representing α/p in terms of X/p .

7. The following expression for \bar{u} in terms of X/α is obtained by eliminating c from the relation (2) and (3)

$$\bar{u} = .307 \frac{X}{\alpha} + \frac{\bar{v}}{2} - \bar{w}y, \quad . \quad . \quad . \quad (4)$$

and it is of interest to find the numbers of electrons with energies above and below the mean value \bar{u} in the space between the two planes $x=a$ and $x=b$.

If $x=a_1$ be a plane near the plane $x=a$, the electrons with the smallest energies which pass the plane $x=a_1$ are those which ionized molecules and the new electrons generated between the two planes. The number ν of these electrons with small energies is $2n_1(e^{(a_1-a)\alpha} - 1)$, n_1 being the total number passing the plane $x=a$. The electrons which ionize molecules just after passing the plane $x=a$ and those they generate have the largest energies in the group ν , and if the maximum energy is equal to \bar{u} the distance $(a_1 - a)$ is given by the equation

$$\begin{aligned} \bar{u} &= X(a_1 - a) + \bar{v}/2 - \bar{w}y \\ &= .307 X/\alpha + \bar{v}/2 - \bar{w}y. \quad . \quad . \quad . \quad (5) \end{aligned}$$

Hence $(a_1 - a) = .307/\alpha$, and the number ν of electrons passing the plane $x = a_1$ with velocities less than \bar{u} is $2n_1(\epsilon^{.307} - 1) = .72n_1$, and the total number passing this plane is $1.36n_1$. Thus 47 per cent. of the total number of electrons passing any plane have energies greater than the mean energy \bar{u} .

After passing through the plane $x = a$ the electrons with the larger energies are the first to ionize molecules, and the others acquire sufficient energy to ionize molecules after moving greater distances through the electric field. The electrons which pass the plane $x = a$ with the energy \bar{u} ionize molecules as the stream passes the plane $x = a_2$, where the total number in the stream has increased to $1.47 \times n_1$. Thus $\epsilon^{(a_2 - a)\alpha} = 1.47$ and $(a_2 - a) = .385/\alpha$. The potential difference between these two planes is $\frac{X}{\alpha} \times .385$, and in helium the value of this potential is 12.3 volts when $X/p = 16$.

Hence, if the energies of the electrons in a group are all nearly equal to the mean energy \bar{u} , when the group is passing a plane $x = a$, the majority of them will ionize molecules near the plane $x = a_2$, which differs in potential from the plane $x = a$ by 12.3 volts when $X/p = 16$. Approximately half the group ionize molecules before and the remainder after passing the plane $x = a_2$.

8. In order to obtain another relation connecting the quantities \bar{u} , \bar{v} , and \bar{v} , independent of the relations (2) and (3), it is necessary to consider the currents in the gas when the electrons set free from the negative electrode first begin to ionize molecules.

When a group of electrons is set free from the negative electrode by ultra-violet light, the same current is obtained for a considerable range of small distances between the plates when the electric force is maintained constant; but as the distance and potential difference between the plates increases beyond a certain point, the electrons acquire sufficient energy to ionize molecules, and the current increases. They all start with a small velocity from the negative electrode, so that comparatively few of the electrons have energies much different from the mean energy of the group in the earlier stages of their motion through the gas. Thus the mean energy of the group may attain the value \bar{u} before ionization by collision begins to have any appreciable effect on the current. Let N be the number set free from the negative electrode, δ_1 their distance from the electrode when their average energy is \bar{u} , δ_2 their distance when half the number in the group N have ionized molecules of the

gas. At this point the number of electrons in the stream is $1.5N$, and the distance δ_2 may be found very accurately from measurements of the currents between the plates at various distances apart when the force X and the pressure p are maintained constant. The preceding investigation shows that if the group of electrons pass the plane $x = \delta_1$ with the mean energy \bar{u} , and half the electrons ionize molecules before reaching the plane $x = \delta_2$, the potential difference between the two planes is $\frac{X}{\alpha} \times .385$. Hence

$$X(\delta_2 - \delta_1) = \frac{X}{\alpha} \times .385 \text{ and } \delta_1 = \delta_2 - .385/\alpha.$$

In moving from the negative electrode to the plane $x = \delta_1$ the electrons lose energy by collisions with molecules, and in the latter part of this path, while their energies increase from $\bar{v}/2$ to \bar{u} , the average loss of energy is $\bar{w}y$. In the first part of the path, before they attain the energy $\bar{v}/2$ they lose a comparatively small amount of energy, which may be denoted as $\bar{w}y'$. Hence, if v_0 be the energy of the electrons when emitted from the negative electrode, the following equation for \bar{u} is obtained :

$$\begin{aligned} \bar{u} &= X\delta_1 + v_0 - \bar{w}(y + y') \\ &= X(\delta_2 - .385/\alpha) + v_0 - \bar{w}(y + y'). \quad . \quad . \quad . \quad (6) \end{aligned}$$

The experiments on the initial development of the current from the constant value N to the value $1.5N$ may also be interpreted as showing that when electrons start with energy v_0 and traverse the distance δ_2 under the force X , they attain the average energy $c + \bar{v}$ required to ionize the molecules. This consideration leads to the following relation between the energies :

$$c + \bar{v} = X\delta_2 + v_0 - \bar{w}(1 + y'). \quad . \quad . \quad . \quad (7)$$

The correction for the loss of energy in collisions with molecules which are not ionized is in this case the same as that occurring in the complete cycle while the energy rises from $\bar{v}/2$ to $c + \bar{v}$, and, in addition, the energy $\bar{w}y'$ lost in the collisions which occur before the electrons attain the energy $\bar{v}/2$.

The expression (6) for u may be obtained by eliminating c and \bar{v} from the equations (2), (3), and (7), so that (6) and (7) are not independent relations between the energies.

In determining the values of the quantities $X\delta_2$ and X/α for substitution in the energy equations, the ratio X/p must

be the same in the various experiments. The same values of $X\delta_2$ and X/α are obtained with different pressures and forces, provided the ratio X/p is constant. With the apparatus which has been used, the distance between the plates was not increased above one centimetre, in order to maintain a uniform electric force between the plates; and the most accurate results are obtained by using comparatively small forces and pressures to determine the potential $X\delta_2$, and forces and pressures about three or four times as large to determine α/p . A full account of these experiments will be given in a future paper, but for the purpose of illustrating the method of obtaining the values of $c + \bar{w}$ and \bar{v} it is sufficient to take the value $X\delta_2 = 30.5$ volts obtained when the ratio X/p is 16.

9. The values of $c + \bar{w}$ and \bar{v} obtained from equations (3) and (7) are :

$$c + \bar{w} = \frac{1.386X}{\alpha} - X\delta_2 - v_0 + \bar{w}y', \quad . \quad . \quad . \quad (8)$$

$$\bar{v}/2 = X\delta_2 - \frac{.693X}{\alpha} + v_0 - \bar{w}y'. \quad . \quad . \quad . \quad (9)$$

The last two terms in these equations are comparatively small, v_0 being about one volt and $\bar{w}y'$ a quantity of the same order, so that for a first approximation to the values of $c + \bar{w}$ and \bar{v} these terms may be neglected. When the values of $X\delta_2 = 30.5$ and $X/\alpha = 32$, which were found experimentally, are substituted in the above equations, the following values of the energies are obtained :

$$c + \bar{w} = 14 \text{ volts}, \quad . \quad . \quad . \quad (11)$$

$$\bar{v} = 16.6 \text{ volts}. \quad . \quad . \quad . \quad (12)$$

It is difficult to obtain accurate evidence from these experiments as to the proportion in which the 14 volts is divided between c and \bar{w} , but it is improbable that the latter quantity is negligible and c is probably not greater than 12 volts. An investigation is being made of the loss of energy of electrons in collisions with molecules of helium by the same method which has been used with air and other gases, and when it is completed it will be possible to make a more accurate estimate of the value of \bar{w} .

The second relation, $\bar{v} = 16.6$ volts, shows that the mean value of the energy of the electrons when they ionize molecules is about 28.6 volts, when the ratio X/p is 16. Hence the energy required to ionize a molecule of helium is approximately 12 volts, and the sum of the energies

of the electron which ionizes the molecule and the electron which is set free is 16.6 volts, after the collision.

In a small proportion of the collisions with energies between 20 and 25 volts, molecules are ionized, but with smaller energies the number which are ionized is inappreciable.

10. There is a considerable difference between the above conclusions and some of those deduced from the valve experiments. It has been found by these experiments that an electron may ionize a molecule of helium by a collision, provided the energy of the electron exceeds a certain minimum value which has been found to be between 21 and 25 volts, and it has been concluded that this number of volts represents the loss of energy of an electron when it ionizes a molecule. This assumption is not, however, supported by experimental evidence, and the direct measurements of the quantity $c + \bar{w}$ obtained from the results of experiments on the conductivity between parallel plates show that c cannot exceed 14 volts.

The valve experiments have also been interpreted as indicating a comparatively large effect due to radiation from the gas, which may be produced by collisions when the energies of the electrons exceed a certain minimum value called the resonance potential, which is less than the ionizing potential. For helium the resonance potential is about 21 volts, and this number of volts is assumed to represent the loss of energy of an electron when it excites molecular vibrations.

The principal difference between the results of the valve experiments and the parallel-plate experiments is in connexion with the radiation effects. Since the resonance potential is less than the ionizing potential, it is reasonable to assume that collisions which give rise to resonance effects occur more frequently than the collisions in which molecules are ionized, while the energy of the electrons is increased from $\bar{v}/2$ to $c + \bar{v}$ under the action of an electric force. Thus the energy \bar{w} lost in collisions with molecules which are not ionized would be very considerable, and the total loss of energy in a cycle ($c + \bar{w}$) would be very much larger than 14 volts.

CIX. *On the Distribution of Energy in the Lines of the Balmer Series of Hydrogen.* By R. T. BEATTY, M.A., B.E., D.Sc.*

IN the March number of the Philosophical Magazine a paper appeared by Prof. P. Lasareff, in which he records visual photometric observations made on a Geissler tube containing hydrogen and excited by a large induction coil. From these observations he obtains the relative energies emitted per second in the lines comprising the first three lines of the Balmer series, and deduces the relative number of atoms which radiate in these three different modes.

This subject was investigated quantitatively some years ago by Jolly† and Beatty‡. Jolly examined a heavy discharge through hydrogen contained in a silica tube by means of a thermopile. In Beatty's work the hydrogen was excited by a constant current which was kept at a low value to diminish absorption of light by the gas, and energies were measured by a photo-electric cell which was calibrated by a thermopile throughout the spectrum. By using water vapour the continuous background was eliminated.

The following table gives Lasareff's results compared with selected values obtained by Jolly and Beatty:—

	Relative energies.		
	Lasareff (1).	Jolly (2).	Beatty (3).
H $_{\alpha}$	1·00	1·00	1·00
H $_{\beta}$	0·34	0·13	0·097
H $_{\gamma}$	0·26	0·053	0·0071
H $_{\delta}$	0·026	0·00093

(1) Heavy disruptive discharge ; current and pressure not measured.

(2) Heavy disruptive discharge with condenser ; current not measured, pressure 29 mms.

(3) Current 15 milliamperes ; pressure 10 mm.

These results differ widely ; this is to be expected, as the relative energies are functions of the pressure and current density. Constant values with a simple interpretation may be looked for only when conditions are such that an atom can emit its full radiation without interference by other atoms, and that absorption of the radiation in the tube can be either measured or eliminated.

* Communicated by the Author.

† Phil. Mag. (6) xxvi. November 1913, p. 801.

‡ Phil. Mag. (6) xxxiii. January 1917, p. 49.

Lasareff, however, disregarding such consideration, has given an interpretation of his results. He argues that since the energy emitted by an atom is $h\nu$, the relative energies in the spectrum lines will give, when divided by the corresponding frequencies ν , the relative number of atoms radiating in each mode.

This argument seems unsound. It neglects the effects of collisions experienced by the radiating atom, the effect of the field of force of neighbouring atoms, the absorption of the radiation by surrounding excited atoms, and the background due to the secondary spectrum of pure hydrogen. It ignores the facts that the relative energies are functions of pressure and current density, that impurities produce a large effect, and that the relative number of atoms and molecules present is influenced by the position of the electrodes and the shape of the Geissler tube.

Much experimental work remains to be done before an answer can be given to the important problem arising out of Niels Bohr's theory of spectra—namely: What is the chance that an atom, which is capable of radiating, shall emit radiation of frequency corresponding to a transition from a given stationary orbit A to another given stationary orbit B?

CX. *The Stark Effect for Strong Electric Fields.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

AFTER a careful study of two papers on the Stark Effect by Mr. A. M. Mosharrafa, which have appeared recently in the *Philosophical Magazine**, I am unable to accept his results without making a small modification. I find that equation (ii.) of the second paper should read

$$N'(n) = (n_1 + n_2 + n_3)^4 \{ 17(n_1 + n_2 + n_3)^2 + 69(n_2 - n_1)^2 - 9n_3^2 \}.$$

Mr. Mosharrafa, in a comparison of the results predicted by his theory with those obtained experimentally by Takamine and Kokubu, finds that the agreement is not as close as could be wished. My results lead to the same value of $N'(n)$ as his, since in all the cases he gives $n_1 = n_2$ and $m_1 = m_2$.

* "On the Appearance of Unsymmetrical Components in the Stark Effect," *Phil. Mag.* May 1922, and "On the Stark Effect for Strong Electric Fields," *Phil. Mag.* August 1922.

But in cases in which the two values of n or m were unequal, the difference would be important.

As pointed out in the second paper, equation (7)* should read

$$B = -\sqrt{A} \left(\sqrt{C} + \frac{nh i}{\pi} \right) + \frac{D}{4A} \left(C - \frac{3B^2}{A} \right) + \frac{5BD^2}{16A^3} \left(3C - \frac{7B^2}{A} \right). \quad (7)$$

Since D^2 contains the factor F^2 , when we substitute for B and B^2 in this equation from (13), we get (to the second order in F)

$$B = -\sqrt{A} \left(\sqrt{C} + \frac{nh i}{\pi} \right) + \frac{D}{4A} \left\{ C - 3 \left(\sqrt{C} + \frac{nh i}{\pi} \right)^2 \pm \frac{F 3h^4 (n_1 + n_2 + n_3) N \left(\sqrt{C} + \frac{nh i}{\pi} \right)}{32m_0 e E^2 \sqrt{A} \pi^4} \right\} - \frac{5D^2}{16A^{5/2}} \left(\sqrt{C} + \frac{nh i}{\pi} \right) \left\{ 3C - 7 \left(\sqrt{C} + \frac{nh i}{\pi} \right)^2 \right\}. \quad (14)$$

Writing in turn

$$\begin{aligned} B &= m_0(eE + \beta), & D &= -m_0 e F, & n &= n_1 \\ \text{and} \quad B &= m_0(eE - \beta), & D &= m_0 e F, & n &= n_2, \end{aligned}$$

and in each case $\sqrt{C} = + \frac{n_3 h i}{2\pi}$ (*cf.* equations (5)), and adding the two resulting equations, we get

$$\begin{aligned} m_0 e E &= -\sqrt{A} \frac{(n_1 + n_2 + n_3) h i}{2\pi} + \frac{m_0 e F (n_1 + n_2 + n_3) (n_2 - n_1) 3h^2}{8A\pi^2} \\ &\quad - \frac{3F^2 h^5 N i (n_1 + n_2 + n_3)^2}{256A^{3/2} \pi^5 E^2} \\ &\quad - \frac{5m_0^2 e^2 F^2 h^3 i}{64A^{5/2} \pi^3} \{ (n_3 + 2n_1)(n_3^2 + 7n_1 n_3 + 7n_1^2) \\ &\quad + (n_3 + 2n_2)(n_3^2 + 7n_2 n_3 + 7n_2^2) \}. \quad (15) \end{aligned}$$

This last cubic in $(n_1 n_2 n_3)$

$$= (n_1 + n_2 + n_3) R,$$

$$\text{where } R \equiv 14n_1^2 + 14n_2^2 + 2n_3^2 + 7n_1 n_3 + 7n_2 n_3 - 14n_1 n_2. \quad (16)$$

* Arabic numerals between 1 and 13 refer to the first of Mr. Mosharafa's papers.

These equations give at once

$$K = \frac{4\pi^2 m_0^2 e^2 E^2}{h^2 (n_1 + n_2 + n_3)^2}, \quad \dots \quad (20 a)$$

$$L = \frac{3h^2 (n_1 + n_2 + n_3) (n_2 - n_1)}{4\pi^2 E}, \quad \dots \quad (20 b)$$

and, after some simplification,

$$M = \frac{h^6 (n_1 + n_2 + n_3)^4}{512\pi^6 m_0^2 e^2 E^4} \left\{ 10R - 54(n_2 - n_1)^2 - \frac{6N}{n_1 + n_2 + n_3} \right\}. \quad \dots \quad (20 c)$$

$$\begin{aligned} \text{Now} \quad N &\equiv (6n_2^2 + 6n_2n_3 + n_3^2)(2n_1 + n_3) \\ &\quad + (6n_1^2 + 6n_1n_3 + n_3^2)(2n_2 + n_3) \end{aligned}$$

(see equation (10), in which there is an obvious misprint of $6n_1n_2$ for $6n_1n_3$),

$$\begin{aligned} &\equiv 3(n_1 + n_2 + n_3)^2 - 3(n_1 + n_2 + n_3)(n_2 - n_1)^2 \\ &\quad - n_3^2(n_1 + n_2 + n_3). \end{aligned}$$

Hence

$$M = \frac{h^6 N'}{512\pi^6 m_0^2 e^2 E^4}, \quad \dots \quad (21)$$

where

$$\begin{aligned} N' &\equiv (n_1 + n_2 + n_3)^4 \{ 140n_1^2 + 140n_2^2 + 20n_3^2 + 70n_1n_3 + 70n_2n_3 \\ &\quad - 140n_1n_2 - 36(n_2 - n_1)^2 - 18(n_1 + n_2 + n_3)^2 + 6n_3^2 \}, \\ &\equiv (n_1 + n_2 + n_3)^4 \{ 17(n_1 + n_2 + n_3)^2 \\ &\quad + 69(n_2 - n_1)^2 - 9n_3^2 \}. \quad \dots \quad (22) \end{aligned}$$

Let W be the energy. Then from equations (5), (20 a), (20 b), and (21),

$$\begin{aligned} W &= \frac{A}{2m_0}, \\ &= \frac{-2\pi^2 m_0 e^2 E^2}{h^2 (n_1 + n_2 + n_3)^2} - \frac{3h^2 (n_1 + n_2 + n_3) (n_2 - n_1)}{8\pi^2 m_0 E} F \\ &\quad - \frac{h^6 N'}{1024\pi^6 m_0^3 e^2 E^4} F^2. \quad \dots \quad (23) \end{aligned}$$

If ΔW denote the change in W due to the introduction of the external field F ,

$$\Delta W = \frac{-3h^2 (n_1 + n_2 + n_3) (n_2 - n_1)}{8\pi^2 m_0 E} F - \frac{h^6 N'}{1024\pi^6 m_0^3 e^2 E^4} F^2. \quad (24)$$

If $\Delta\nu$ be the corresponding change in frequency, Bohr's

formula gives us

$$h\Delta\nu = \Delta W_m - \Delta W_n, \quad \dots \quad (25)$$

where W_m , W_n denote the energies in paths characterized by quantum numbers $m_1 m_2 m_3$ and $n_1 n_2 n_3$ respectively.

$$\begin{aligned} \text{Thus} \quad \Delta\nu = & \frac{3hF}{8\pi^2 m_0 E} [(n_2 - n_1)(n_1 + n_2 + n_3) \\ & - (m_2 - m_1)(m_1 + m_2 + m_3)] \\ & + \frac{h^5 F^2}{1024\pi^6 m_0^3 e^2 E^4} [N'(n) - N'(m)]. \quad (26) \end{aligned}$$

Balliol College, Oxford,
10th February, 1923.

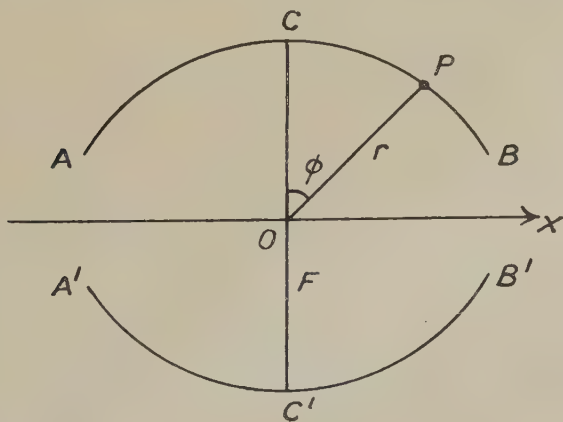
Yours truly,

H. O. NEWBOULT.

CXI. *The Spectrum of the Semi-circular Helium Model.*

By H. O. NEWBOULT, B.A., Scholar of Balliol College, Oxford*.

SOME time ago Langmuir put forward a model of the helium atom, in which the electrons vibrate about the nucleus in opposite directions†. In the accompanying diagram, the orbits are ACB, A'C'B', and they are reflexions



of each other in an axis Ox , through the nucleus O . By the method of successive approximations and mechanical integration, Langmuir showed that the orbit ACB is very nearly an arc of a circle, whose centre F lies on the perpendicular to Ox through the nucleus.

* Communicated by Dr. J. W. Nicholson, F.R.S.

† See the Physical Review, 2nd Series, xvii. p. 339.

The ordinary Sommerfeld-Wilson quantum condition $\int p dq = nh$, when applied to this model, gives a negative value for the ionizing potential, and therefore the model is untenable unless the quantum conditions are modified. Langmuir suggested that the maximum angular momentum of a single electron should be set equal to $\frac{h}{2\pi}$, and deduced as the value of the ionizing potential 25.62 volts, in close agreement with the experimental value of $25.4 \pm .25$ volts obtained by Franck and Knipping.

Langmuir does not discuss the question of the spectrum of helium; but if his hypothesis is correct, it would appear that the spectrum should be obtained by setting the maximum angular momentum of an electron equal to an integral multiple of $\frac{h}{2\pi}$. In this model it is clear that the maximum angular momentum of the electron which vibrates in the path ACB is attained at the middle point C. If OC is r_0 and the angular velocity at C is $\dot{\phi}_0$, we obtain as our quantum condition,

$$m_0 r_0^2 \dot{\phi}_0 = \frac{n h}{2\pi}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where m_0 is the mass of an electron, and n is an integer.

Now, Langmuir proves that if $-W$ is the total energy of the system,

$$\frac{W r_0}{e^2} = 2N - \frac{1}{2} - \alpha, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where Ne is the nuclear charge and

$$\alpha = \frac{m_0 r_0^3 \dot{\phi}_0^2}{e^2}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and obtains as the value of α ,

$$\alpha = 2.0920. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

From (1) and (2) we get

$$m_0 r_0 e^2 = \frac{n^2 h^2}{4\pi^2 \alpha}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and from (2), on putting $N=2$ for helium,

$$\begin{aligned} W &= \frac{e^2(7-2\alpha)}{2r_0}, \\ &= \frac{2m_0 e^4 \pi^2 \alpha (7-2\alpha)}{h^2} \frac{1}{n^2}. \quad . \quad . \quad . \quad . \quad (6) \end{aligned}$$

Hence the frequency of the spectrum should be given by

$$\nu = \frac{\alpha(7-2\alpha)2m_0\pi^2e^4}{h^3} \left(\frac{1}{m^2} - \frac{1}{n^2} \right),$$

$$= \alpha(7-2\alpha)R \left(\frac{1}{m^2} - \frac{1}{n^2} \right), \quad . \quad . \quad . \quad . \quad (7)$$

where R is the Rydberg constant and m and n are integers.

The formula (7) cannot accord with the ordinary series in the spectrum of helium; but this fact would not preclude the temporary existence of helium atoms of the structure considered in sufficient numbers to show perhaps a weak spectrum. Thus a test of the formula numerically is desirable in order to determine whether it can lead to any lines associated with helium but not belonging to the ordinary series.

$m.$	$n.$	$\lambda.$	$\nu.$
3	4	3183.83	31408.8
4	5	6878.64	14537.8
4	6	4457.36	22434.8
4	7	3676.94	27196.5
4	8	3301.74	30287.0
5	6	12662.9	7897.06
5	7	7899.68	12658.7
5	8	6349.51	15749.2
5	9	5596.57	17868.1
5	10	5158.98	19383.7
5	11	4821.02	20505.1
5	12	4682.10	21358.0
6	7	21001.0	4761.68
6	12	13460.9	7428.92

The values of m and n in the table were selected with a view to obtaining wave-lengths in the visible spectrum. The first line and the last two show that such lengths can only be given by $m=4$ or 5 .

The spectrum does not show a correspondence with any known spectrum; and the only conclusion that can be made is that the hypothesis about the quantum condition used in Langmuir's investigation is not correct, though it does lead to a suitable value of the ionizing-potential.

CXII. *Adsorption from the Gas Phase at a Liquid-Gas Interface.*—Part I. By THOMAS IREDALE*.

IT was proposed to measure the adsorption at a liquid-gas interface of a substance which is present, not in solution in the liquid phase but as a constituent of the gas phase only. The idea is not new (Gibbs, *Scientific Papers*, vol. i. p. 235; Cantor, *Annalen der Physik*, vol. lvi. p. 492, 1895; Langmuir, *Journ. Amer. Chem. Soc.* vol. xxxix. p. 1848, 1917), but has never been given any quantitative expression. From measurements of the surface-energy changes of a liquid under varied pressures of an adsorbed vapour, the amount of the adsorption might be calculated from the Gibbs equation (*l.c.*), $\Gamma = -\rho \frac{d\sigma}{dp}$,

but the actual measurement of the adsorption itself is of much greater difficulty. Very few such measurements are to be found in the literature, the more notable ones being those of Donnan (*Proc. Roy. Soc. A*, vol. lxxxv. p. 558, 1911) and Lewis (*Phil. Mag.* 1908, p. 499, and 1909, p. 466; *Zeit. Phys. Chem.* vol. lxxiii. p. 129, 1910), which were concerned with the adsorption at liquid-gas and liquid-liquid interfaces respectively of substances in solution in the liquid phase. There exist, however, very considerable discrepancies between the experimental values for the adsorption and those calculated with the aid of the Gibbs equation. One reason for this is probably the fact that the substances employed were either electrolytes or organic substances of high molecular weight which tended to form colloidal solutions, and one could not be sure that the gas laws were obeyed with sufficient accuracy, and there was also the difficulty of a probable irreversible gelatinization of the colloid at the interface. The adsorption of a gas or vapour is free from such defects as these, though in the latter case the interesting phenomenon of incipient condensation must not be overlooked.

The first part of this investigation is concerned with a suitable method of measuring the surface tension of a liquid under the prescribed conditions—*i. e.*, a continuously varying vapour phase.

The Drop-weight Method of measuring Surface Tension.

In view of the recent developments of the technique of this method (Harkins and co-workers, *Journ. Amer. Chem. Soc.* vol. xxxviii. p. 839, 1916; vol. xli. p. 499, 1919; vol. xlii. p. 2534, 1920), it was decided to employ it in the preliminary investigations, and, if necessary, to use some

* Communicated by Prof. F. G. Donnan, F.R.S.

other method later as a check on the results. A careful examination, however, of the recent work in this field has convinced the writer that the drop-weight method, though quite satisfactory practically if the procedure of any particular worker be followed rigidly, does not yet rest on a really rational basis. It would seem that as far back as 1881 (Worthington, *Proc. Roy. Soc.* vol. xxxii. p. 362, 1881) and later (Guye and Perrot, *Archives des Sc. Phys.* vol. xi. p. 225, 1901; vol. xv. p. 132, 1903) more was known about the actual conditions of drop formation and detachment than the modern experimenter is aware of, and that in the curious mathematical developments of the original formula much has been assumed but very little explained.

The only reasonable formula for a *cylindrical* drop hanging from a tube under the influence of gravity is the one quoted by Worthington and Lord Rayleigh (*Phil. Mag.* (5) vol. xlviii. p. 321, 1899), namely $w = \pi r T$, where w is the weight of the drop, r the radius of the tube, and T the surface tension. This is an equilibrium condition, and a slight increase in w should result in a detachment of the drop. This, however, never happens, for, by reason of its rapidly changing shape, the drop takes up new positions of equilibrium, and finally detaches at a stage quite beyond our control (Lohnstein, *Ann. Physik*, vol. xx. pp. 237, 606, 1906). The above formula has therefore to be modified by a correction factor, which varies according to the shape of the drop. This is the method that Harkins has adopted in his more recent measurements, but for some reason or other he prefers to use the formula $w = 2\pi r T$; and although this gives correct results in the end, as his method is purely a comparative one, it must be admitted that the whole procedure is far from satisfactory. His definition of an ideal drop, as one conforming to that formula, seems without meaning, and can only be used as a convenient standard for want of a better understanding of the real facts of the case.

There was another formula developed in Worthington's day (Worthington, *l. c.*) which rests on a sounder theoretical basis, and seems to the author to explain in a much more logical manner the more accurate results of the modern experimenter. The fact that it did not come into general use is due to that very reason—that no experimental data in those days were sufficiently accurate to test its validity. Harkins (*l. c.*), for instance, has shown how unsatisfactory were Rayleigh's results, due to the use of thin-walled tubes. The formula is a comparative one, and rested on the assumption at the time, and is certainly in agreement with the

interesting fact at the present day, that different liquids may form drops of similar shape from tubes of different diameters.

If T_1 , T_2 be the surface tensions, ρ_1 , ρ_2 the densities of two liquids, and K the ratio between two similar linear dimensions of the drops—*e. g.*, the ratio of the radii of the tubes from which they hang, or of the principal radii of curvature,—then the equation of symmetry becomes

$$K^2 = \frac{T_1 \rho_2}{T_2 \rho_1}.$$

A satisfactory proof of this equation has already been given by Worthington, and it will not be necessary to repeat it here; but it will be seen that it affords a most convenient method of calculating the surface tension of any liquid of known surface tension and density. For if, by choosing a suitable radius of tube in both cases, the drops of the two liquids can be made to assume similar shapes, then the value of K , the ratio of the two radii, can be ascertained; and that is all that is required now for the solution of the equation. It is yet to be explained, however, in what way it is possible to ascertain the exact shape of the drop and its variation with the size of the tube employed. Now it is a remarkable fact that the shape of a drop is completely decided by the ratio of the radius of the tube to the radius of the detached portion of liquid considered as a sphere, and although this is purely an experimental fact, there are some theoretical reasons for assuming that this must be the case. If the equation of symmetry is to have any significance at all, it must hold right down to the moment of detachment of the drops; and as the rupture undoubtedly occurs at the point of maximum concavity*, the same fraction of the hanging drop will detach in the two cases; and, moreover, the radii of the spheres which the detached element of fluid immediately forms will bear the same ratio to the radii of the two tubes. Consequently, if we have a small and a large drop, of different liquids but of the same shape, and we imagine them projected on to a screen, both to the same size, then we could not distinguish between the mode of detachment in the two cases, and the projections of the falling spheres would have the same radius.

We have assumed that the rupture occurs at the point of maximum concavity, as it is here that any upward force due to the surface tension is least; and though the cohesive forces of the liquid are now the deciding factors in the detachment,

* Guye and Perrot, *Arch. des Sc. Phys.* vol. xiii. p. 178 (1903).

the fact that these vary from liquid to liquid does not appear to affect the argument. It follows also, from the conditions of symmetry, that the ratio between the distances of these points of maximum concavity from the bases of the drops must have the value K , which is determined entirely by the surface tensions and densities of the liquids forming the drops.

All that is required now is a knowledge of the tube-radius and drop-radius ratio, with a continuously varying radius of tube, for some standard liquid of known surface tension and density.

The most complete and accurate data for this purpose are supplied by Harkins and Brown (*Journ. Amer. Chem. Soc.* vol. xli. p. 499, 1919), who measured the weights of drops of water falling from tubes of all radii, from 0.09 to 1 cm. The author has calculated the radius of the drop in each case and the ratio it bears to the radius of the tube from which it falls, and the results are given in Table I. and expressed

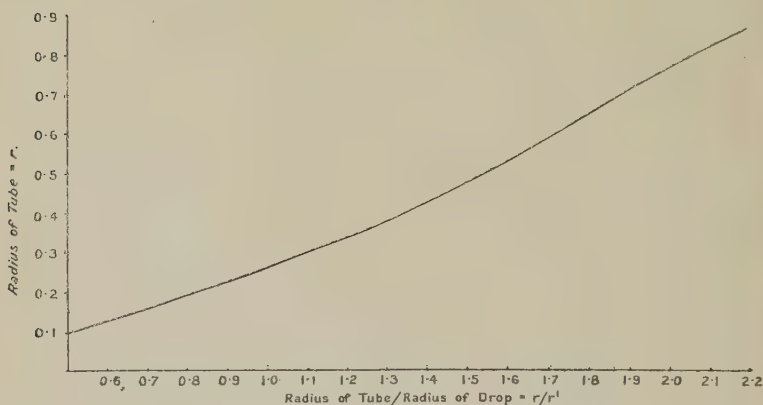
TABLE I.

Radius of tube. r .	Radius of drop. r' .	Ratio. r/r' .
0.09946 cms.	0.1998 cms.	0.4977
0.14769 "	0.2238 "	0.6603
0.19666 "	0.2425 "	0.8112
0.23052 "	0.2532 "	0.9103
0.23790 "	0.2555 "	0.9863
0.26802 "	0.2645 "	1.014
0.27605 "	0.2669 "	1.035
0.29423 "	0.2719 "	1.081
0.29694 "	0.2727 "	1.088
0.31891 "	0.2785 "	1.145
0.32362 "	0.2797 "	1.157
0.34188 "	0.2844 "	1.202
0.37964 "	0.2938 "	1.289
0.39262 "	0.2970 "	1.322
0.44755 "	0.3103 "	1.442
0.50087 "	0.3231 "	1.551
0.55009 "	0.3351 "	1.643
0.59703 "	0.3463 "	1.724
0.65031 "	0.3581 "	1.816
0.69883 "	0.3692 "	1.894
0.72229 "	0.3744 "	1.929
0.74784 "	0.3780 "	1.978
0.77329 "	0.3829 "	2.019
0.79915 "	0.3854 "	2.073
0.84894 "	0.3888 "	2.184
1.0028 "	0.3900 "	2.571

graphically in fig. 1. It will be seen that the ratio varies in a continuous and gradual manner, and passes through unity for one particular radius of tube.

It will be shown now how, with the aid of Table I. and the equation of symmetry, the surface tension of any liquid may be found, provided its density is known. The weight of a drop of the liquid falling from a tube of known radius is first ascertained, from which its radius, and hence the ratio of the tube-radius to the drop-radius, can be calculated. By referring to the table, the radius of the tube corresponding to this ratio in the case of water can be found. In the equation of symmetry the value of K is the ratio of this

Fig. 1.



tube-radius for water to the tube-radius for the other liquid, and since T_1, ρ_1 the surface tension and density of water, and ρ_2 the density of the liquid are known, its surface tension T_2 is thus easily evaluated. The computation seems a little puzzling at first, but in practice is really very simple and rapid, and gives just as accurate results as any calculation involving the notion of "ideal drops" or the use of various mathematical functions.

To take some concrete cases:—The weight of a drop of mercury falling from a capillary tube, the radius of the bore being 0.0852 cm. (r), was found to be 0.1794 gram at 25° C. The density of mercury at this temperature is 13.53; hence the radius of the drop is 0.1469 cm. (r'); whence $r/r' = 0.5801$. Referring to Table I., we can calculate that, to give this ratio, the radius of the tube for

water must be 0.1239 cm. The value of K is therefore given by $1239/852$, and since $T_1=72.8$, $\rho_1=0.998$, and $\rho_2=13.53$, T_2 has therefore the value 466 dynes per centimetre.

Harkins (Journ. Amer. Chem. Soc. vol. xli. p. 513, 1919) gives 0.025783 gram as the weight of a drop of benzene falling at 20°C . from a tube of radius 0.23052 cm. The density of benzene at this temperature is 0.897, and by making a similar calculation the surface tension of benzene is found to be 28.92 dynes per cm. [Richards's (Journ. Amer. Chem. Soc. vol. xxxvii. p. 1656, 1915) and Harkins's (*l. c.*) values vary from 28.88 to 28.94 dynes per cm.]

It is essential in all drop-weight determinations that the period of drop formation be fairly long—a matter of minutes,—or that the nearly full-sized drop be allowed to hang for some time, and the detachment effected by very gradual increments of fluid. This is not only to allow sufficient time for surface equilibrium to be reached, especially when we are dealing with a definite adsorption phenomenon, but also to prevent an undue dynamical effect, caused by the too rapid entrance of fluid into the drop. For the same reason, vibration must be avoided as much as possible, as secondary droplet formation might occur and vitiate the results.

It is obvious that this method is applicable to the case of a drop hanging in another liquid of less density than itself; and ρ_2 in the formula becomes then the apparent density of the drop, and the case of a drop detaching upwards in a liquid of greater density than itself could also be catered for by a slight modification of the formula.

The "drop symmetry" method of measuring the surface tension of liquids depends, then, on the conformity of the latter to certain definite principles which, as far as the author is aware, are in the majority of cases followed with remarkable exactness. But it is obvious that liquids of extremely high viscosity, or with a tendency to gelatinize, may have to be excluded from the present considerations; and the difficulty that many of these have in forming drops of definite shape precludes them in any case from all drop-weight methods of measuring surface tension.

The three postulates on which the "drop symmetry" method depends may be re-stated finally as follows:—

- (i.) That it is possible for different liquids to form drops of similar shape when emerging from tubes of different diameters.

- (ii.) That drops of the same shape, which have assumed similar forms continuously to the point of rupture, will detach in similar ways.
- (iii.) That, in the case of all such similar drops, the radius of the tube from which they hang bears a constant ratio to the radius of the detached element of fluid, considered as a sphere.

The principle of symmetry lies at the basis of all comparative drop-weight methods, and, as outlined in the present paper, seems to the author to offer the most satisfactory explanation of the recent accurate experimental results.

Adsorption from the Gas Phase.

This form of adsorption was originally considered by Gibbs (*l. c.*) for the case of mercury and water vapour. Owing to the abrupt change in density of the mercury from the liquid to the gaseous phase, the original equation of equilibrium simplifies to $\Gamma = -\rho \frac{d\sigma}{dp}$, where Γ is the surface excess of adsorbed vapour, ρ the density of the vapour, and $\frac{d\sigma}{dp}$ the rate of change of the surface tension of the mercury with the partial pressure of the vapour. This equation may be deduced in a more simple manner, though by no means as rigidly as in Gibbs's original method, in the following way:—

If we take p and s as the independent variables defining the system (for a given temperature), and if F denote the thermodynamic potential (ζ function of Gibbs), then

$$\delta F = v\delta p + \sigma\delta s,$$

where σ is the interfacial tension.

Hence

$$\left(\frac{\partial v}{\partial s}\right)_{p,t} = \left(\frac{\partial \sigma}{\partial p}\right)_{s,t}.$$

But

$$\rho\delta v + \Gamma\delta s = 0,$$

where Γ = excess concentration of vapour per unit area of interface,

and ρ = density of vapour in the vapour phase.

Hence

$$\left(\frac{\partial v}{\partial s}\right)_{p,t} = -\frac{\Gamma}{\rho},$$

and therefore

$$\Gamma = -\rho \left(\frac{\partial \sigma}{\partial p}\right)_{s,t}.$$

Adsorption of Organic Vapours by Water.

A number of preliminary experiments have been carried out on the influence of the vapours of certain organic liquids on the surface tension of water.

For this purpose an ordinary dropping pipette was constructed, having a tip made of capillary tube. By means of a constriction in the top of the pipette the drops were made to take at least twenty seconds to form at the tip, and the number obtained from a given volume of water in the pipette, which changed a great deal when the drops were formed in the presence of the vapours, served to indicate the surface tension of the water.

It has been found that the more soluble a substance is in water, the greater is the effect of its vapour on the surface tension of this liquid. Substances such as pentane or hexane, which on shaking with water give solutions having surface tensions very little different from the surface tension of pure water, yield vapours at 20° C. influencing the surface tension to the extent of from 5 to 10 per cent. Substances such as chloroform or methyl acetate have a much greater effect than this, and in addition are much more soluble, their solutions having considerably lower surface tensions than pure water. For the purpose of the present investigation, only substances of very slight solubility could be considered as serviceable, and this seemed to restrict one to the use of the saturated hydrocarbons. As pure specimens of the latter were difficult to obtain, research in this direction has been abandoned for the time being, though it must be admitted that the study of the adsorption of hydrocarbon vapours by water is of peculiar interest and importance, as we are dealing with substances of a non-polar character and anticipate a quite distinct type of adsorption layer.

Adsorption of Organic Vapours by Mercury.

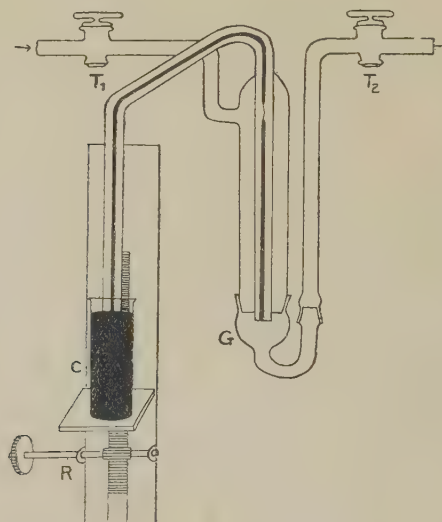
The vapours of all organic liquids seem to have the property of lowering the surface tension of mercury.

In the study of this phenomenon a special apparatus was devised (fig. 2) which, so far, has worked satisfactorily. The dropping pipette consists, as usual, of capillary tube, with a very narrow constriction at one place to slow down the rate of movement of the mercury column, and with a specially prepared tip. This latter was made, as recommended by Harkins (*l. c.*), by filling the capillary with Wood's metal and grinding to a level surface with emery. Rouge was used for the final polishing, and then the Wood's metal

was melted out, and the orifice cleaned with nitric acid and examined under the microscope. For the purpose of accurately measuring the diameter of the orifice a travelling microscope was employed, and a sample of capillary tubing was rejected, in the first instance, if its bore was at all elliptical in cross-section, though it is remarkable that some portions of tubing have so perfectly circular a bore that the slight irregularity, if such exists, is not detectable to within 0.0003 cm. under the microscope.

The rate of formation of the drop is dependent on the difference in height of the orifice of the pipette and the

Fig. 2.—Drop-weight apparatus.



mercury in the container C; and by means of the rack-and-pinion device R, this container can be raised or lowered and the period of drop formation controlled to a nicety. It can be varied from a few seconds to half an hour, and the nearly full-sized drop can be allowed to hang for an even longer period if necessary.

The apparatus was placed in an air thermostat regulated to 0°·1 to 0°·2 C., and the rack-and-pinion device worked from outside. The air in the thermostat was stirred by means of a fan worked by an electric motor, and although the latter was supported on a framework attached to the wall of the room, some vibration was communicated to the thermostat,

and as a check on the results, the fan was sometimes shut off for a few moments before the drop detached. Slight errors caused by small vibrations are not appreciable ; but it may be found necessary, where extremely great accuracy is required, to eliminate even the imperceptibly small vibrations. The drops, as they detached, fell into the removable cup G and were afterwards weighed.

Where it was found necessary to employ a lubricant for the taps, etc., dextrin dissolved in glycerin was used.

In these preliminary experiments, organic vapours mixed with air have been employed. This procedure seems justifiable from certain evidence which will be submitted later.

The vapours were generated by passing a very slow current of dry air at constant pressure through the organic liquids in series of saturators of a type similar to that described by Cumming (*Trans. Faraday Soc.* vol. vi. p. 10, 1910). That efficient saturation was obtained may be judged from the fact that when the temperature of the thermostat was $0^{\circ} \cdot 2$ C. below that of the saturators, visible deposition of liquid occurred on the walls of the glass drop-weight apparatus in the thermostat, and when the temperature of the latter was $0^{\circ} \cdot 2$ C. above that of the saturators no such deposition could be observed.

The following was the procedure adopted in every case:—After the current of vapour had been flowing through the apparatus for some time, the tap T_2 was closed and the current shut off. The vapour in the apparatus was now allowed to acquire the temperature of the thermostat (26° C.), which in some cases was considerably above that of the saturators ; but the vapour pressure is decided entirely by the temperature of the liquid in the saturators, and the only difficulty we are concerned with is that the vapour cannot quite reach the temperature of the thermostat while in thermal communication with a portion of its containing vessel at a much lower temperature. This difference, however, was not very great as a rule, and the temperature of the mercury, which is a much better conductor of heat, is really the deciding factor in the adsorption.

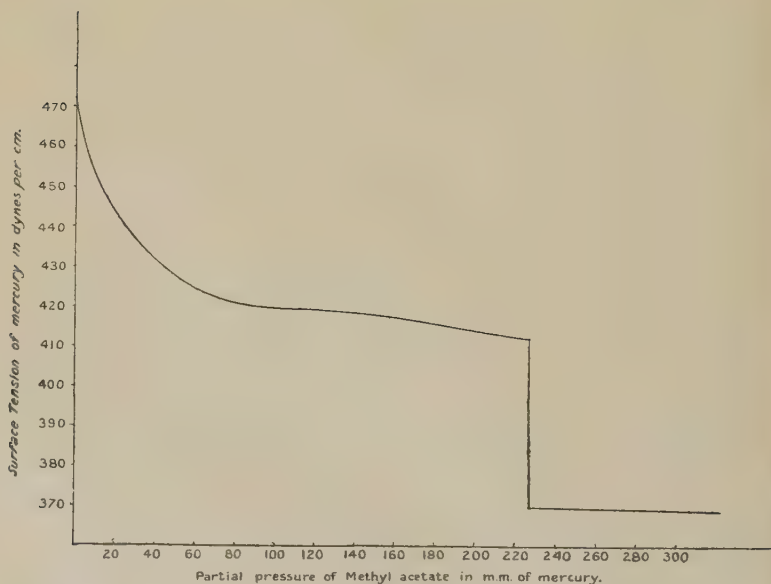
The period of drop formation was never at any time less than three and a half minutes, and with longer periods the weights of the drops were not found to decrease appreciably. The adsorption of the vapour appear, then, to be a fairly rapid process.

The surface tension of mercury in air varies a great deal according to the amount of moisture in the atmosphere. When a current of dry air is passed through the drop-weight

apparatus, as high a value as 472 dynes per cm. has been obtained, which is very little different from the surface tension *in vacuo*.

It was not anticipated, then, that the air present with the organic vapour would interfere very much with the adsorption of the latter. This is an important point, as Stockle's results (Wied. Ann. vol. lxvi. p. 49, 1898) seem to indicate that the presence of air and other gases interferes with the formation of a surface equilibrium with mercury, though only when a dynamical effect is considered. Now that the drop-weight method of measuring surface tension has become practically a statical one, these effects, of course, are not readily observed.

Fig. 3.



The type of curve obtained when the surface tension of mercury is plotted against the varying partial pressures of organic vapour is shown in fig. 3 and is obtained from the data in Table II., the organic liquid in this instance being methyl acetate.

[The mercury was purified by treatment with dilute nitric acid and distillation in a current of air.

The methyl acetate was purified from a commercial sample by treatment with potassium carbonate solution and fractionation after standing over phosphoric oxide.]

TABLE II.

Temperature of saturators.	Vapour pressure of methyl acetate.	Drop weight.	Surface tension of mercury.
—	0 mm.	0.1903 gram.	472 dynes per cm.
-20.0° C.	19 "	0.1780 "	444 " "
0 "	62 "	0.1685 "	423 " "
10.8 "	109 "	0.1673 "	419 " "
15.0 "	137 "	0.1665 "	418 " "
18.3 "	157 "	0.1658 "	417 " "
26.0 "	227 "	0.1640 "	412 " "
	(saturated vapour)	to 0.1454 "	to 370 " "

(Diameter of orifice of drop-pipette = 0.1796 cm.)

After a certain vapour pressure is reached [the vapour pressures were obtained from Young and Thomas's data (*Journ. Chem. Soc.* vol. lxiii. p. 1209, 1893) for methyl acetate], saturation with an adsorbed film occurs, and the curve becomes practically horizontal. But the phenomenon does not end here. As the temperature of the saturators approaches that of the thermostat, the value of the surface tension suddenly falls; but this seems to depend on certain conditions which are, as yet, outside the control of the experimenter. Two figures are therefore given for the surface tension in the saturated vapour: the highest obtainable, which is near the value for the saturated adsorption; and the lowest, which is practically the value of the surface tension of mercury in liquid methyl acetate. The rest of the curve is hypothetical, and merely indicates that the surface tension at the interface of the two liquids considered does not alter much with increased pressure. This makes up the complete form of the curve, but the most interesting parts of it are the first three—namely, a phase of increasing adsorption, a saturation phase, and a condensation phase.

A calculation from the formula $\Gamma = -\rho \frac{d\sigma}{dp}$ of the adsorption for a vapour pressure of 62 mm. leads to a value for Γ of about 4.5×10^{-8} gram of methyl acetate per square centimetre. It can be further calculated from this result that the number of methyl-acetate molecules per square centimetre of mercury surface is 0.37×10^{15} . It seems, then, that in all probability we have a monomolecular layer, as this figure is very near the values given by Langmuir (*Journ. Amer. Chem. Soc.* vol. xxxviii. p. 2288, 1916) for monomolecular layers of carbon dioxide, nitrogen, etc.

Moreover, the space taken up by each molecule (27×10^{-16} sq. cm.) is near that required for molecules of esters and fatty acids on the surface of water, namely 23×10^{-16} sq. cm., and it is possible that the same type of orientation obtains on the mercury surface.

There appears, however, to be a somewhat abrupt change from a simple adsorption process to a condensation, and this phenomenon is now being investigated in greater detail.

I am indebted to Professor Donnan for suggesting to me the idea of this research and for the great interest he has taken in its progress, and to the Royal Commissioners of the 1851 Exhibition for a scholarship which is enabling me to continue the work.

Physico-Chemical Laboratory,
University College, London,
March 20, 1923.

CXIII. *Notices respecting New Books.*

Prolegomena to Analytical Geometry in Anisotropic Euclidean Space of Three Dimensions. By ERIC HAROLD NEVILLE, late Fellow of Trinity College, Cambridge and Professor of Mathematics in University College, Reading. Cambridge University Press, 1922. 30s. net.

IN a stimulating volume, Professor Neville has given an account of the principles underlying the use of Cartesian axes and vector frames in ordinary space and of ideal complex Euclidean space of three dimensions. In the first section the Author deals with various fundamental matters such as, for example, attaching signs to the volume of a tetrahedron, matters in the discussion of which it is of great importance to avoid ambiguity. The next section is concerned with vector analysis and gives an account of the development of the subject. The exposition is very clear, and the logical status and the characteristics of a vector—a complex in which a number is associated with a direction—are developed in a manner which, quite apart from the uses to which the theory of vectors is put in subsequent sections of the volume, is of great value in that it affords an admirable example of the modern logical method in mathematics which was introduced by Frege and Russell. The next section applies vector analysis to obtain formulæ for use with Cartesian axes and with vector frames; the next deals with the construction of algebraic space, and the final section with ideal space.

There are two aspects from which the present volume might be discussed. As regards the actual progress of geometry, it is evidently of great importance that the attention of students of geometry should be directed towards the problems which are here

discussed. Quite apart from the particular treatment accorded to them in this book, it is of real value to have the problems stated clearly and incisively.

On the other hand, the careful study of this book will repay students of mathematics who wish to understand something about the structure of mathematics. The method of definition and the logical development of the characteristics of vectors adopted here show clearly the kind of way in which any body of mathematical knowledge must finally be built up. The building-up of any domain of knowledge can, of course, only come after the new ideas have been conceived and the discoveries have been made. Once the material exists, even if it exists only in the form of isolated results, the building-up of the results into a new domain of knowledge can only be accomplished by the careful critical development of the characteristics of concepts defined in abstract terms. The present work enables us to see this building process in operation. As an example of the logical method at its best, Professor Neville's work can be enthusiastically recommended.

D. M. W.

British (Terra Nova) Antarctic Expedition 1910-1913. I. *Determinations of Gravity*: 4to, pp. 105+plates 4; 7s. 6d. net.
II. *Observations on the Aurora*: 4to, pp. 46+plates 2; 7s. 6d. net. By Capt. C. S. WRIGHT. Harrison & Sons.

THE first of these papers is an account of the determination of the value of gravity at Cape Evans during the last Scott Antarctic Expedition. It deals mostly with the experimental methods employed. The result is that the value of gravity at Cape Evans, 10 feet above sea-level, is $983.003 \pm .002$ cm/sec². The observations seem to have been carried out with remarkable care and precision in the difficult circumstances. To indicate the kind of difficulties that had to be faced, one may mention that hoar frost, largely from the observer's breath, was formed on the optical parts of the apparatus, and the temperature was so low that a wait of about two weeks was necessary for this to evaporate. On the other hand, the low temperature was found useful in the construction of a support for the pendulums: the freezing of water in the interstices of gravel produced a quite satisfactory concrete. The result will be of much use in investigations of the figure of the earth: observations at more stations would, of course, be required before we could reach any conclusion about the isostatic compensation of the Antarctic Continent. Other determinations were made at Christchurch, Wellington, and Melbourne, and the whole checked against Potsdam.

The auroral observations were made at Cape Evans and Cape Adene, and have been analysed with regard to the diurnal variation and the relation to terrestrial magnetism. They cannot be discussed satisfactorily in a short abstract; the paper will be a valuable source of information to investigators of polar phenomena.

H. J.

Tables Annuelles Internationales de Constantes et Données Numériques de Chimie, de Physique et de Technologie. Vol. IV. Parts 1 and 2 (2 volumes). Gauthier-Villars (Paris); Cambridge University Press (Cambridge); University of Chicago Press (Chicago), 1922.

THE publication of these valuable tables was interrupted by the war. The two volumes now issued are evidence of the great effort which is being made to deal effectively with the vast mass of material which has accumulated since the appearance of the last volume in 1914. They cover the years 1913 to 1916 inclusively; Volume V., which is announced to be in preparation, will carry the work up to the end of 1920.

Wherever we have consulted the tables, we have found them very complete as far as the period covered is concerned. The arrangement, however, still leaves something to be desired: for instance, data covering the X-ray spectra are to be found in Part 1 under the general heading *Spectres d'émission*, subheading *Emissions de rayons X*, and different data for the same period in Part 2 under the heading *Rayons Roentgen*, subheading *Spectres de rayons Roentgen*. This particular case is not of great practical importance, because all workers are aware that the data given have by now been mostly superseded by more refined measurements, but it indicates a need of more careful classification. It is, however, ungracious to find minor faults in a performance of such difficulty as the assemblage and arrangement of these masses of tables at the present time. To get some idea of the labour involved, it is only necessary to glance at, say, the section dealing with magnetism. We feel that all physicists will congratulate M. Marie, the general secretary, and his collaborators on the appearance of these volumes, and do their best to give what help they can to promote the speedy appearance of Volume V. All communications on the subject of the tables are welcomed by the secretary.

We would like to suggest that it would be acceptable to working physicists if the latest values of all the universal constants could be assembled together, instead of being scattered under various headings.

X Rays. By G. W. C. KAYE. Fourth Edition. Longmans, 1923. Price 16s.

DR. KAYE'S excellent little book, dealing in an elementary manner with all aspects of X rays, has now gone into a fourth edition. There have been no essential changes made, but fresh matter has been added on the practical uses of X rays, including both the industrial applications and the work done on old pictures by Drs. Heilbronn and Chéron, in which advantage is taken of the different X-ray absorption of different pigment layers to reveal details which have been painted over. The only criticism which

we have to offer of the new edition does not affect Dr. Kaye: it is that, in spite of the much enhanced price, the book is not so well produced as was the first edition.

The Principle of Relativity with applications to Physical Science. By A. N. WHITEHEAD. Cambridge University Press. Price 10s. 6d.

PROFESSOR WHITEHEAD in this volume has put forward an alternative rendering of the Theory of Relativity which calls for careful and thorough examination.

The first part deals with general principles of a philosophical nature. It carries a good deal further the inquiry undertaken by the author in his two previous works 'The Principles of Natural Knowledge' and 'The Concept of Nature,' and it should be read in connexion with them. In this discussion of the character of our knowledge in general and of our knowledge of nature in particular, the author comes to the conclusion that our experience exhibits and requires a basis of uniformity—a uniformity which in the case of nature exhibits itself in the uniformity of spatio-temporal relations. This conclusion is in severe disagreement with the spirit of Einstein's second theory, and Professor Whitehead's searching analysis and detailed working-out of his own point of view which is grounded in these philosophical premisses is consequently of the greatest interest. A second fundamental divergence from conventional Relativity is to be found in the view of the inter-relation of physics and geometry which is here expounded. One of the most novel parts of the theories of Einstein is the suggestion that different types of geometry can be made to absorb different types of physical force. The large step from the first theory of Relativity of 1905 to the second of 1915 consists largely in the suggestion that a certain specific type of geometry can be made to absorb gravitational fields. In the present volume, however, a very different view is taken. Physics and Geometry are considered to be fundamentally distinct. The point of view adopted is developed with the admirable logical skill always to be found exhibited in the works of the author from premisses suggested by general philosophical considerations.

These important divergences from orthodox Relativity theory as it has grown up during the last eight years call for detailed consideration. The great skill of the author as a mathematician and a logician, and in particular as a Geometer, make this book an important challenge to Relativists in general. It is unnecessary to describe the method of treatment of the present volume otherwise than by referring to the author's international reputation as a keen thinker whose splendid work in these domains has done much to initiate a new epoch in the logic of science.

CXIV. *Intelligence and Miscellaneous Articles.*

THE REACTION CONSEQUENT UPON THE EVAPORATION OF A LIQUID AND UPON THE EMISSION OF VAPOURS FROM SMALL ORIFICES.

[The following addition to Professor Duffield's paper under the above title reached us after our April number was published. It should be added at the end of Section 4 on p. 676.—Eds.]

WE may, I think, obtain some indirect evidence concerning the rate at which the molecules of a vapour issue from a boiling liquid, from a series of observations made by Royds (Phil. Trans. Roy. Soc. A, 1908) upon the mechanism of the electric spark. Using a method devised by Schuster and Hemsalech, he photographed the spectrum of the spark upon a rapidly-moving film and obtained lines drawn out into streamers, whose inclination gave a measure of the velocity of the material in terms of the velocity of the film. In all cases they were greatest close to the pole; the maximum velocities measured may be taken as approximating to the velocities of projection.

In the accompanying table we compare these velocities, $v_{\text{obs.}}$, with those of atomic agitation, v_{T} , of the material of the poles, on the assumption that the temperature, T , of the hot pole is that of the boiling-point, as it almost certainly is in the arc. For this purpose we use the equation $v_{\text{T}} = v_{\text{H}} \times \sqrt{2/273} \times \sqrt{T/M}$, where v_{H} is the velocity of the hydrogen molecule (18.39×10^4 cm./sec.) and M is the atomic weight of the material. We see from the table that the two velocities are of the same order of magnitude; indeed, considering the difficulties in the measurements, the agreement is remarkable. In some cases two types of lines were distinguished by Royds, and designated by him Types I. and II.; usually the former give velocities rather less, and the latter velocities greater than v_{T} . Royds regards the streamers as being charged negatively, but I think the only evidence in favour of this is that they seem to emanate from the pole which is momentarily the cathode; it may, however, well be that only the cathode is raised to the boiling-point. Since the velocities fall off as the vapour reaches the centre of the gap, it is clear that the atoms are *projected*; they do not start from rest and accelerate under the forces of the field, but rather diffuse into the surrounding vapour. There is some reason for thinking that the streamers are rendered visible by fast-moving electrons projected from the cathode at the same time that the vapour is emitted.

Taking the agreement between calculated and observed values of the velocities in conjunction with other indications, the view is strengthened that molecules are projected from a boiling liquid with their temperature velocities.

Element	Mg.	Al.	Zn.	Cd.	Sn.	Sb.	Hg.		Pb.		Bi.	
Type	I.	II.	I.	I.	II.	II.	—	—	I.	II.	I.	II.
Velocity obs., $v_{\text{obs.}}$...	4.6	8.7	3.9	4.0	13.7	22.3	9.4	11.5	3.0	19.6	2.8	20.2
„ calc., v_{T}	11.9	13.7	6.7	4.8	7.2	5.9	2.8	2.8	3.6	3.6	4.5	4.5
Ratio, $v_{\text{T}}/v_{\text{obs.}}$	2.6	1.6	1.7	1.2	.5	.3	.3	.3	1.2	.2	1.0	.2